SOME BIOGENIC COMPOUNDS AND THEIR DERIVATIVES IN SELECTED MANGROVE ECOSYSTEMS

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Certificate

This is to certify that this thesis entitled "Some biogenic compounds and their derivatives in selected mangrove ecosystems" is a bonafide record of the research work carried out by Smt. Rini Sebastian under my supervision and guidance in the Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, in partial fulfilment of the requirements for the degree of Philosophiae Doctor of the Cochin University of Science and Technology and no part thereof has been presented before for any other degree, diploma, associateship, fellowship or any other similar title or recognition.

Kochi – 682016
December 2002

Dr. Jacob Chacko
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DECLARATION

I hereby declare that this thesis entitled "Some biogenic compounds and their derivatives in selected mangrove ecosystems" is an authentic record of the research carried out by me under the supervision of Prof. (Dr.) Jacob Chacko, Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, in partial fulfilment of the requirements for the Ph.D. degree of Cochin University of Science and Technology and that no part of it has previously formed the basis for award of any degree, diploma, associateship, fellowship or any other similar title or recognition in any University.

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Dedicated To

My Parents

Husband & Lenoy

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1.1 MANGROVES

"If there are no mangrove forests, then the sea will have no meaning. It is like having a tree with no roots, for the mangroves are the roots of the sea" (MAP, 1999). Mangroves are important, complex and dynamic ecosystems, occurring in thick fringes in the intertidal zone along tropical and subtropical coastlines. This unique ecological niche is inhabited by a variety of plants and animals, which utilize the environment for food, shelter and reproduction. Ong (1982) has commented, "The mangrove is nature's own aquaculture system with a number of advantages like it is more stable and less susceptible to disease and epidemics."

1.1.1 Mangrove Ecology

Mangrove forest generally embodies two different concepts. Firstly it refers to an ecological group of evergreen plants belonging to several families but possessing marked similarity in their physiological characteristics and structural adaptation to similar habitat preferences. Secondly, it implies a complex of plant communities fringing sheltered tropical shores with a rich diversity of both floral and fauna resources. Mangrove plants are adapted for growth in a saline environment on loose wet soil that is periodically submerged by tides.

1.1.2 Mangrove Zonation

Mangrove systems are classified on the basis of physical appearance (forest structure), hydrology, and productivity. Riverine forests, the most productive, are those that lie along river and creek channels. These forests are the largest in stature and experience a constant flow of water both in the dry season (through daily tidal activity) and wet season (from terrestrial runoff). Fringe forests are moderately productive intertidal mangrove wetlands that occupy protected shorelines and the mouths of channels. Fringing mangroves are known for their capacity to trap sediments from both marine and terrestrial sources. Overwash forests are subtidal to intertidal marine-dominated systems that have productivity values resembling fringe forests. This forest type is commonly found in the form of a small island that is constantly washed by tides. Basin forests are also moderately productive forests that are found in more inland areas. These mangroves are rarely inundated by tidal action nor terrestrial runoff. Dwarf (scrub) forests are the least productive. This

forest type is dominated by a stunted form of mangrove (usually Rhizophora mangle). These wetlands, although long in hydroperiod, are low in both nutrients and hydrologic energy. Hammock mangrove wetlands appear as tree islands along fringing coastlines. They grow in depressions and have characteristics similar to basin and dwarf mangroves (Lugo and Snedaker, 1974).

1.1.3 Mangrove Environment

Plants which grow in areas of tidal influence must be able to deal with environmental extremes not experienced by other plants.

Direct effect of the tide - Plants growing in the lower portion of the tidal range have their root systems covered by water at least twice a day. Water logging displaces air from the soil and effectively prevents diffusion of oxygen through the spaces in the soil. One of the most obvious effects of the tide is the regular replenishment of the soil water across the whole area. Where water logging occurs, the soil rapidly becomes anoxic and takes on the typical sulphide smell of the mangrove swamp. This is a natural phenomenon due to the restriction of oxygen supply by water logging and the presence of bacteria which carry out anaerobic forms of respiration where sulphur is the final electron acceptor and is not due to pollution or environmental degradation.

Salinity of water - Mangrove plants live in an environment having salinity equal to or greater than that of seawater. Mangroves, being quite large trees, require a plentiful supply of water. The water which evaporates from their leaves is pure but the water which is available to their roots contains a large amount of salt.

1.1.4 Morphology and physiology of mangroves

Since they lie at the interface of land and sea, mangrove wetlands, like salt marshes, display ranges in salinity from fresh to brackish to marine (and even to hypersaline in highly evaporative areas). Mangrove species dominate these ecotones because they have evolved several mechanisms that allow them to be successful under these highly variable salinity regimes (Chapman, 1976; Clough, 1984).

Although regularly inundated with seawater, mangroves live in a 'dry' environment as a desert. When the salt content of the surrounding water is high, the plant will lose water out of its cell. When water evaporation rates are high, there is

a deficiency of water. The plants close their stomata to reduce further water loss, which also halts the uptake of carbon dioxide and reduces photosynthesis. This problem of obtaining water is termed "physiological dryness".

Mangroves are termed facultative halophytes. This means that while they can grow in salt water, they can also do well in freshwater. They generally do not thrive in freshwater because competition from other species crowds them out. i.e., one particular advantage to growing in a salty environment is the lack of competition. Only a limited number of plants have invested evolutionary energy into adapting to such harsh conditions. In the optimum conditions of a tropical rainforest, diversity is great and competition fierce.

Mangroves have two internal methods to survive in the saline environment. They can either exclude salt (not take it into the plant), or extrude salt (take salt in, transport it up their trunks and dispense it through glands in their leaves).

Salt excluder - Some separate freshwater at the root surface by means of a non-metabolic ultra filtration system. This reverse osmosis process is powered by high negative pressure in the xylem resulting from transpiration at the leaf surface. Some species can exclude more than 90 per cent of salt in sea water. (Rhizophora, Ceriops, Bruguiera and Osbornia species are all 'salt-excluders'.)

Salt extruders - Another method, is to quickly excrete salt which has entered the system. i.e., regulating ionic concentration by extruding salt through glands on the leaf surface. This is a temperature sensitive enzymatic process, and requires that energy be spent to actively transport sap. The leaves of many mangroves have special salt glands which are among the most active salt-secreting systems known. (Examples of 'salt-secreters include Avicennia, Sonneratia and Acanthus.)

A third method of coping with salt is to concentrate it in bark or in older leaves which carry it with them when they drop. (Lumnitzera, Avicennia, Ceriops and Sonneratia species all use this trick).

As can be seen from the examples given, some mangroves use only one of these methods but many use two or more. In addition, a number of features serve to conserve water. These include a thick waxy cuticle (skin on the leaf) or dense hairs to reduce transpiration - the loss of water. Most evaporation loss occurs through

stomata - pores in the leaves - so these are often sunken below the leaf surface where they are protected from drying winds. Leaves are also commonly succulent, storing water in fleshy internal tissue.

Roots - One of the characteristics of mangroves is the development of roots, which are exposed to air, at least at low tide. These allow gas exchange in roots systems in substrates that are generally anoxic and waterlogged. Many species have highly specialised roots structures, which are typical of particular genera. These can be divided in four types; stilt roots, pneumatophores, knee roots and buttress roots.

Stilt roots (drop roots) - Stilt roots are characteristic of Rhizophora, but also occur in Brugeria and Ceriops. They may also occur in Avicennia alba and A. officinalis. They grow downwards from the trunk and branches, providing water uptake in the sections below the sediment. They also possess many lenticels for the exchange of gases needed for respiration and will enable the tree to root even in mud lacking oxygen for diffusion of gases. Once aerial roots extend into the bottom they will provide adequate protection from displacement and ensure the continuing subsistence of the plant. Thus they provide support in older trees. They are also known as aerial roots or prop roots.

Pneumatophores - Pneumatophores project through the sediment surface from underlying cable roots and function primarily in gas exchange. They are characteristic of Avicennia and Sonneratia.

Knee and blade roots - Knee roots are raised loop sections of cable roots, with thickening on the upper exposed side, forming "knees". These are characteristic of species of Brugueira and Ceriops.

Buttress or plank roots - In Xylocarpus granatum, horizontal cable roots develop vertically blade growth along their length, forming extended blade or plank roots above the sediment surface. Similar development from the base of the trunk in Heriteira species results in the development of buttress roots.

Germination - Through "viviparity," embryo germination begins on the tree itself; the tree later drops its developed embryos, called seedlings, which may take root in the soil beneath. Viviparity may have evolved as an adaptive mechanism to prepare the seedlings for long-distance dispersal, and survival and growth within a

harsh saline environment. During this viviparous development, the propagules are nourished on the parent tree, thus accumulating the carbohydrates and other compounds required for later autonomous growth. The structural complexity achieved by the seedlings at this early stage of plant development helps acclimate the seedlings to extreme physical conditions which otherwise might preclude normal seed germination. Many mangrove species including Bruguiera, Ceriops, Kandelia, and Rhizophora, display vivipary. Another special adaptation is the dispersal of certain mangroves' "propagules" which hang from the branches of mature trees. These fall off and eventually take root in the soil surrounding the parent tree or are carried to distant shorelines. Depending on the species, these propagules may float for extended periods, up to a year, and still remain viable. Viviparity and the long-lived propagules allow these mangrove species to disperse over wide areas.

1.1.5 Mangrove diversity

Three mangrove species dominate the wetland areas, the red mangrove (*Rhizophora mangle*), black mangrove (*Avicennia germinans*) and white mangrove (*Laguncularia racemosa*). The red mangrove is the tallest, with recorded heights of 25 m. The leaves are long (12 cm), waxy, dark green above and pale below. The roots, trunk and branches have a thin grey bark covering a dark red wood. Notable characteristics include the prop roots derived from the trunk and drop roots from aerial branches. Small yellow flowers are most common in the summer, but the long (15 cm), cigar shaped propagules may be found hanging on the tree at any time of the year.

The second tallest species is the black mangrove, which may reach heights of 20 m. The small (10 cm) leaves are elliptical or oblong, and green on the upper surface. The undersurface is covered with dense hairs often encrusted with salt. The bark is dark and scaly. This tree displays distinctive aerial roots (pneumatophores), which stick up from the ground like thin fingers. Flowering occurs during summer months, and result in bean-shaped propagules (2-3 cm long) in late summer and early fall.

The white mangrove is the smallest of the three mangroves (sometimes it appears to be a shrub) with maximum heights of 15 m. It has broad, flat oval leaves

up to 7 cm long that are rounded at both ends. Two salt glands are found at the base of each leaf at the apex of the petiole. Flowering occurs in mid to late summer and produces very small (<0.5 cm) propagules resembling peas a month later.

1.1.6 Physical Functions and Economic Value

Mangroves provide a wide variety of direct and indirect services to society and the economy. Mangroves are vital natural systems that need to be protected as a near shore nutrient source, as breeding, feeding and nursery grounds of marine organisms, and for land building, stabilization and protection purposes. Their importance to biological, chemical, physical and geological processes occurring in the coastal zone is evident (Kristensen et al., 1991; 1992; Alongi et al., 1992; 1993; Woodroffe, 1992; Robertson et al., 1992; Hemminga et al., 1994).

Sediment Stabilisers - The mangrove plants are important stabilisers of fine sediments, with a substantial amount of sediment being deposited with each retreating tide. The algae on the surface of the mud help to bind together sediment particles, and soil is also trapped between roots. They act as a buffer against coastal erosion.

Nutrient Sink - Mangrove, and the sediments associated with them, can assimilate substantial quantities of nutrients such as nitrogen and phosphorus, thereby preventing contamination of nearshore waters and may reduce the incidence of eutrophication and possibility of red tides (Robertson et al 1992). Toxins may also be retained in mangrove and associated sediments. Mangroves have also been useful in treating effluent.

Biodiversity and Genetic Value - Primary mangrove is reasonably diverse, and is habitat for several endangered species. Mangroves are physiologically unique in their ability to live in salt and brackish water.

1.1.7 Mangrove use

Mangrove forests have been widely and variously used by the people who live in or close to them and who traditionally have made a living from the mangrove ecosystem for thousands of years. Mangroves are so productive that they are the source of livelihood for many people. The wide variety of traditional products from mangroves utilised by coastal communities is well-documented (Bandaranayake,

1998). Basic necessities such as food, shelter, fuel, and medicines are all obtained from mangroves. Some mangrove products have been useful to man in the past. Fruits of the red mangrove are edible, and the leaves have been used for tea, medicinal purposes and as livestock feed. The wood from the red mangrove is durable and water resistant, and has been used for boats, houses, pilings, fence posts and furniture. Black mangrove flowers produce nectar for honey, and the bark has been used for tannin and dyes. The dense wood of the black mangrove and buttonwood has been burned for charcoal. Traditionally the mangroves of India and Bangladesh have been exploited for timber and fuelwood, bark tannin, animal fodder, native medicines and food (fish, shellfish, honey, wild animals). Many of these activities still continue, and include collection of thatching material (Nypa), gathering of shells to produce lime and wild honey collection (in the Sundarbans especially). Mangrove timber has always been important to traditional coastal communities for house and boat building (FAO, 1982), and remains so today. The importance of bark tannins has declined in many Asian countries, but some mangrove tannin is still used in India and Bangladesh for leather curing and there are some other traditional uses, e.g. for curing fishing nets in Sri Lanka (FAO, 1982). The gathering of mangrove leaves (Avicennia) for animal fodder remains widespread in the Middle East and Southern Asia, for feeding camels in Iran and India, for example; in fact grazing by domestic animals is a serious cause of mangrove degradation in parts of India. Mangrove honey is an important economic product extracted from the Sundarbans (Bandaranayake, 1998). Although impossible to quantify, hunting also remains a significant activity in the Sunderbans and in many other areas in Asia where mangroves are still extensive.

Numerous medicines are derived from mangroves. Skin disorders and sores, including leprosy, may be treated with ashes or bark infusions of certain species. Headaches, rheumatism, snakebites, boils, ulcers, diarrhoea, haemorrhages and many more conditions are traditionally treated with mangrove plants. The latex from the leaf of the blind-your-eye mangrove (Exoecaria agallocha) can indeed cause blindness, but the powerful chemicals in it can be used on sores and to treat marine stings. Mangrove plants are a rich source of steroids, triterpenes, saponins, flavonoids, alkaloids and tannins (Bandaranayake, 1998). The use of saponins as natural detergents and fish poison were known to the primitive people. The

interesting pharmacological properties associated with the Chinese drug "ginseng", which is considered a panacea and a drug for longevity, are attributed to the various saponins present in it. Plant saponins have other interesting biological activities such as spermicidal (Kamboj et al., 1976) and molluscicidal (Marston and Hostettmenn, 1985), antimicrobial, inflammation-inhibiting, antiviral, analgesic, antifungal, mosquito larvicidal, piscicidal and cytotoxic activities (Mahato et al.,1988; Bandaranayake, 1998). Their potential value as cytotoxic and antineoplastic agents and as antimicrobial agents, for example in wood preservation or prevention of dental caries has been demonstrated (Scalbert, 1991). Novel inhibitors of HIV-1 reverse transcriptase have been characterized from the Malaysian tree *Calophyllum inophyllum* (Patil et al., 1993). Chemicals identified from *Calophyllum inophyllum* are prospective lead compounds for anticancer drugs (Tosa et al., 1997).

1.2 DISTRIBUTION OF MANGROVES

1.2.1 Global distribution of mangroves

Mangroves once covered 3/4 of the world's tropical coastlines. Asia contains most of the world's mangroves with 46%, followed by America with 35% and Africa with 17% (MAP, 1999). Mangrove wetlands are the salt marshes of tropical and subtropical regions of the world. They are most commonly found along favorable coastlines between 25°N and 25°S latitude (Kuenzler, 1974). World wide, during 1980's the mangrove forest covered about 24 million hectares and are found in the coastal zones of sub-tropical and tropical countries (Twilley et al., 1992). According to Spalding (1997), the total area of mangroves in the world is approximately 181,399 sq.km. Furthermore, the largest mangrove area occurs in Indonesia, (30%) Brazil (10%) Australia (8%) and in India only (3%). The mangrove ranges differ globally quite clearly regarding numbers and diversity of species. Indian ocean and the pacific region have a large diversity of species whereas low diversity of species distinguish the America and West Africa regions (Jordan, 1991). Most of the species belong to the families of the *Combretaceae* followed by *Rhizophoraceae* and *Avicenniacea*. According to Aksornkoae (1995), 79 mangrove species are found in the world.

Substantial areas of mangrove forest occur in Asian countries like Pakistan, India, Bangladesh, Myanmar, Thailand, Cambodia, Vietnam, Malaysia, Philippines and Indonesia. About two fifth of all mangrove forests in the world occur in Asia. The major mangrove forests of South and Southeast Asia can be divided into two broad groups. The mangroves of South Asia are dominated by non-rhizophore species while the most dominant and commercially important species in the mangrove forests in Southeast Asian countries are a number of species from the family Rhizophoraceae.

1.2.2 Status of Mangroves in India

The coastal areas of India accommodate about one fourth of country's population that is dependent to a large extent on marine resources. On the Indian coast, mangroves are found along the islands, major deltas, estuaries and backwaters and constitute an important resource in India. Like terrestrial tropical forests, mangroves have been a significant part of the Indian economy for thousands of years and are a reservoir of valuable natural resources. Mangroves constitute a significant portion of the coastal wetlands on which a large percentage of coastal population is depended directly or indirectly.

In India, the mangrove forest covers about 360,000 ha (Govindasamy and Kannan, 1996). Sunderbans is the largest single block of mangrove forest in the South East Asian Region occupying about 4000 square kilometres. Mangrove areas of lesser extent of 5000-15000 hectares are encountered elsewhere in the estuaries of Mahanadi, Godavari, Krishna, Cauvery and along smaller river systems and salt water creeks along the west coast. The Andaman-Nicobar islands contain some of the least disturbed.

A total of 65 mangrove species is recorded throughout India. Of these, 62 are found in the Sundarbans, 63 in Mahanadi delta, 29 towards the Godavari- Krishna-Cauvery and west coast region and 30 in the Andaman and Nicobar Island. The dominant mangrove species are Rhizophora, Bruguiera, Sonneratia and Kandalia.

1.2.3 Status of mangroves in Kerala

According to authentic records, about 70,000ha of mangroves which once fringed the backwaters of Kerala, have now been reduced to a few isolated patches

consisting of a few species. The important mangrove patches existing now in Kerala are scattered across the state at Veli, Quilon, Kumarakom, Kannamali, Mangalavanam, Vypeen, Chetwai, Nadakkavu (Calicut), Edakkad, Pappinisseri, Kunchimangalam and Chittari (Ramachandran et al., (1986). Mangroves and associated species reported include *Sonneratia caseolaris, Kandelia candel, Bruguiera sp., Lumnitzera racemosa, Excoecaria agallocha, Aegiceras sp., Ardisia littoralis* (unique to Kerala mangals), *Caesalpinia crista, Dolichandron spathecea, Heritiera littoralis, Phoenix humilis var. pedunculata, Flagellaria indica, Viscum orientale, Derris trifoliata, Dalbergia candenatensis, Dendrophthoe falcata, Acampe praemorsa, Samadera indica, Hopea ponga, Phragmitis karka, Cyperus javanicas, Paspalam vaginatum, Carallia brachiata, Syzygium travancorium* (unique to Kerala mangals), *Premna serratifolia, Morinda citrifolia, Scalvola serica, Acrostichum aureum.*

The mangroves in and around Greater Cochin comprise of woody species such as Avicennia, Rhizophora, Bruguiera, Excoecaria etc. and shrubby forms like Acanthus, Clerodendoron, Aegicaras, etc. and also a mangrove fern Aerostichum aureum. Towards the land ward fringes, mangrove associated ferns like Thespesia populnea, Hibiscus tiliaceous, Terminalia catappa, Pandarus sp., Artocarpus spp. are often encountered. Towards the beach side of lagoons, strand vegetation such as Ipomoea pescaprae, Acanthus sp., Panicum spp. are common. From the Cochin estuary, *Acanthus ilicifolius*, *Rhizophora* sp. and *Bruguiera* sp. were reported (Naskar and Mandal, 1999).

1.3 MANGROVE DESTRUCTION

1.3.1 Causes for the deterioration of mangroves

The mangrove ecosystem is a very dynamic one, where changes are taking place regularly, and within the range of mangrove habitats most major species grow within a given set of conditions. Any major changes in these conditions may start to bring about changes in the growth pattern of different species, a complete elimination of one or more species resulting from changes in the composition of the forests, or in extreme cases a complete disappearance of the forest. Because of this severe sensitivity to change in habitat conditions, mangrove forests are very

susceptible to destruction. Human activities create stress on the ecosystem beyond its tolerance limit that can pose hazards to the coastal and marine environment, and to the health and safety of the population living in the coastal areas.

The causes of mangrove destruction around the world are many. They may be classified as: overexploitation by traditional users; conversion to aquaculture; conversion to agriculture; conversion to salt pans; conversion to urban development; construction of harbours/port and channels; mining; liquid waste disposal; solid waste of garbage disposal; oil spillage, and other hazardous chemicals. Natural stresses such as cyclones and freshwater discharges also destroy mangrove forests, but the areas are minimal compared with those lost from human activity.

The mangroves, with their swampy soils, clusters of breathing roots, prop roots and tangle of trees and twiners have often been considered as a waste land or dangerous place inhabited by harmful wild animals. Mangroves are often thought of as smelly, grassy "wastelands" cut by numerous channels, oozing with mud, and often swarming with blood-sucking insects and thus their intrinsic values have often been overlooked when any development activity is undertaken due to compulsions of population pressure and the consequent socio-economic development needs. In the past, mangrove areas were generally regarded as useless and hostile territory. Because of their bad reputation, mangroves are the ecosystems most in danger of disappearing. Despite their significance, these ecosystems at frequently at great risk in both developed and undeveloped countries. Regardless of the social circumstances, the habitat is often regarded as prime for conversion to some other use and may be indiscriminately cleared for industrial, agricultural or residential purposes.

Mastaller (1996) have shown that in Kerala, which once boasted of having about 70000ha. of mangrove, what remaining is only 250ha. i.e. only 4% of the initial area is remaining within the period 1911-1989. The Cochin Backwater was originally fringed by mangroves and was famous for prawn fishery; the mangroves were cut down to convert the backwater to agriculture farms or purposes. Mangroves have been ruthlessly felled because of their prime seafront location.

1.3.2 Ecological and Economical Impacts of Mangrove Destruction

Although mangrove systems are floristically "simple" compared to other tropical forests, they have complex trophic structures and intricate interrelationships among physical, chemical and biological components that are not well understood. Thus, a change in a single component may not necessarily cause immediate change in ecosystem function, but continued pressure on this component may eventually alter ecosystem function through feedback effects on other components and processes.

Mangrove forest tends to react sensitively towards disturbances from outside the system. The major problems associated with indiscriminate use of the coastal wetlands are increasing soil acidification, loss of nutrients, soil erosion, and decreasing fishery potential, which in turn have led to many ecological and economic problems along the coast (Untawale, 1992). Mangrove destruction may lead to a reduction in the number of species or number of individuals in large water birds and mammals, mass fish mortality and decreasing levels of spawning in fish and prawns. Inevitably most people living in or associated with mangroves suffer economic losses once this ecosystem is disturbed or eliminated. The destruction of mangrove ecosystems, the local fisheries is affected, economically and socially. Industrial fisheries experience a decline in near shore fish and shrimp catches which are directly or indirectly linked to the status and spatial extent of tidal forests. On a global scale, the loss of mangrove wet lands means a loss of critically important wet land for many migratory species. Theories of global warming, polar cap melting and coastal flooding have been linked to global rain forest destruction and consumption of fossil fuels.

Deterioration of soil (acid sulphate soils) - Mangrove soils developed from sea water sediments contain high sulphides which occur in the form of iron sulphide (FeS) and pyrites (FeS_2). Drainage of mangrove soil for agricultural purposes and the exposure of the pyretic sediments during excavation of ponds lead to their oxidation, resulting in the formation of sulphuric acid which is released in the soil, thereby increasing the acidity of the soil, and in such cases pH may drop below 3.0 (Alongi et al., 1998). Under conditions of severe acidity, solubility of aluminium, iron and manganese increases and this may cause phytotoxicity. This creates a situation where the substrate becomes toxic to the growth of any

organism. At low pH the availability of nutrients also decreases greatly and important nutrients become unavailable to plants, and as a result, soil fertility is greatly reduced. Acid sulphate soils with low pH are toxic to the growth of both plants and animals and most plants and animals, invertebrates and fish die at high levels of acidity. At moderate levels of acidity, the rate of growth of plants and production of fish and other organisms are substantially reduced. In case of reclaimed rice fields, the production of rice decreases gradually with each crop while acidity steadily increases. The same is true in the case of fish and shrimp ponds, where with increased acidity the production level falls steadily. At some point soon the agriculture/aquaculture practices do not remain viable and are abandoned, because of unfavorable growing conditions created by the toxicity. As strongly acid sulphate soil is unable to support any vegetation, the barren soil becomes highly degraded and is prone to erosion.

Erosion - Drainage of mangrove forest after clearance, together with breakdown of the root system, results in land subsidence and leaves soils that are susceptible to erosion.

1.4 MANGROVE PRODUCTIVITY

The mangrove ecosystem is a good example of how each part is dependent on the whole for survival. Mangrove ecosystems are among the most productive ecosystems and their carbon stock per unit area can be enormous (Twilley et al., 1992). Mangrove communities produce much of the essential nutrients to support the organisms comprising the low end of the food chain, and support both large and small food webs. Mangrove plants produce litter (mainly leaves, twigs, bark, fruit and flowers) some of which is consumed by crabs but most must be broken down before the nutrients become available to other animals. Bacteria and protozoa colonize in the plant litter and break it down chemically into organic compounds, minerals, CO_2 and nitrogenous wastes. They feast on the litter, increasing its food value by reducing unusable carbohydrates and increasing the amount of protein - up to four times on a leaf which has been in seawater for a few months. Amphipods and other small grazers speed up this reduction process by shredding the litter. This increases the surface area, which aids microbial colonization and speeds up decomposition. In seawaters, where shredding organisms such as crabs and

amphipods are active, decomposition is faster than in freshwater or dry conditions. Faster decomposition is also apparent with an increase in tidal fluctuation. The resultant detritus, enriched nutritionally by its microbial population, is a food source for a variety of organisms. Partly decomposed leaf particles, loaded with colonies of protein-rich micro-organisms, are then eaten by fish and prawns. They in turn produce waste which, along with the smallest mangrove debris, is munched up by molluscs and small crustaceans. Even dissolved substances are used by plankton or, if they land on the mud surface, are browsed by animals such as crabs.

The plants and animals found in a salt marsh are a unique assemblage of terrestrial and aquatic species, as the salt marsh is an 'overlap zone' between the land and the sea. The important associated species are bacteria, fungi, algae, bryophytes/ferns lichens, monocotyledons, dicotyledons, sponges/bryozoa, coelenterata/ctenophora, non-polychaete worms, polychaetes, crustaceans, insects/arachnids, molluscs, echinoderms, ascidians, fish, reptiles, amphibians, birds and mammals. Many annelid worms, clams, mussels, snails, smaller crustaceans etc. depend wholly on detritus for their diet. Terrestrial animals enter the salt marsh at low tide, including native rat species, snakes, while birds such as ibis, herons and spoonbills feed on prawns and shrimps in pools of water.

In general, Red mangroves have the greatest net production, Blacks intermediate, and Whites the lowest figures of net primary production. Primary consumers are the decomposers.

Regularly influenced and disturbed by seasonal freshwater and diurnal tidal flooding, mangrove forest exhibits features of an immature ecosystem, namely low species diversity and high productivity. Mangroves are among the most productive ecosystems and play a key role in the coastal food chain and nutrient cycles (e.g. Robertson & Alongi, 1992). They are believed to enhance near-shore primary and secondary production (Mann, 1982). The shallow mangrove waters, abundance of food, and absence of predators are ideal for young organisms to thrive. Underneath the mangroves, soft soils provide an excellent habitat for burrowing prawns and other mud dwellers. The nutrient rich layer provides food for the herbivores found in the mangroves. Detritus and dissolved organic and inorganic nutrients exported from mangroves provides a major energy source in tropical coastal waters to support high productivity in food chains involving large numbers of detritus-

feeding species, such as mullets and penacid shrimp. This release of excess nutrients is essential for resources such as oysters. Many high value, commercially exploited fish and shellfish utilize mangroves during part of their life cycles.

Although shelter from predators or special food requirements could possibly be amongst the reasons for the type of migration, it appears more likely that such migration is worth while only if productivity in mangroves is greater than that in the sea, and there is good reason to believe that this is indeed the case. In mangrove swamps, primary productivity can be attributed to several sources: the mangrove tree themselves, from their associated attached macrophytic vegetation and algae, from free-floating macrophytic vegetation, and from phytoplankton or benthic microalgae. On the marine system, on the other hand, primary productivity can only come from the last of these sources and from seaweeds and seagrasses if they happen to be present.

1.5 ORGANIC COMPOUNDS IN MANGROVE ECOSYSTEMS

Mangrove swamps are example of estuarine ecosystems that receive large quantities of senescent leaf material that are an important source of carbon and other nutrients to food webs and to pools of dissolved and particulate organic matter. The decomposition of mangrove leaf material occurs primarily through microbial action and the leaching of water-soluble compounds. During the initial stages of decomposition, large quantities of dissolved organic matter (DOM) leach from decaying leaves resulting in a rapid massive loss (Benner et.al.1988). Waters in the vicinity of decaying leaves are often "tea–coloured" due to the relatively high concentrations of DOM that contains tannins and other phenolic compounds. After the initial leaching phase, rates of mass loss from the remaining leaf material are much lower (Woodruffe, 1982; Benner & Hodsen, 1985). The remaining leaf material has been presumed to be composed primarily as structural polysaccharides and lignin. Mangrove plant tissues are important sources of organic matter and often rich in tannin and polymethylene – type polymers that are likely precursors of geopolymers such as humic substances and kerogens (Benner et al., 1990b).

1.5.1 Types of Organic Compounds

- ***Carbohydrates***

Carbohydrates are important structural and storage components of aquatic organisms. They exist as monosaccharides, disaccharides, trisaccharides, polysaccharides etc. They are important carbon and energy sources for microheterotrophs in both freshwater and marine ecosystems (Romankevich, 1984; Thurman, 1985) and contribute essentially to the bacterial production (Hanisch et al., 1996; Rich et al., 1996). Carbohydrates are some of the major biochemicals produced by living organisms, and constitute an important fraction of dissolved, particulate and sedimentary organic matter (Skoog and Benner, 1997; Borsheim et al., 1999; Burdige et al., 2000). The extracellular degradation of macromolecular POC to a range of organic carbon intermediates is an important part of sediment carbon remineralization (Henrichs, 1992; Burdige and Gardner, 1998), and carbohydrates are known to be produced and consumed as intermediates during remineralization (Boschker et al., 1995; Arnosti and Holmer, 1999).

Due to the high percentage of structural carbohydrates in vascular plant tissues, most carbon and energy flow results directly from the oxidation of carbohydrates. Storage carbohydrates such as starch and sucrose, which play critical roles in cellular metabolism, also contribute to the total carbohydrate reserves in plants (Loewus and Tanner, 1981). Additionally, certain carbohydrates are either peripheral or integral components of other major compounds such as lignins and tannins (Sjøström, 1981; Zucker, 1983).

Despite the well-recognized importance of carbohydrates in the aquatic carbon food web, there is surprisingly little information about the insitu composition, concentrations and dynamics of the different fractions of the carbohydrates such as monosaccharides and the polysaccharides in dissolved and particulate forms as well as in sediments. As compared with other regions, very little information is available on the distribution of sugars in the mangroves of Cochin.

- ***Amino acids and Proteins***

Amino acids are the building blocks of protein in living biomass. In the aquatic environment most of the amino acids occur as polymers. Proteins are

formed by condensation of amino groups and carboxyl groups of α-amino acids to form a peptide bond. Amino acids, the components of proteins, are essential organic nitrogen compounds in living organisms (Lehninger 1972). In the aquatic environment, amino acids account for 13% to 45% of the particulate organic carbon flux and 31% to almost 80% of the particulate organic nitrogen flux (Lee and Cronin 1982; Ittekkot et al., 1984a,b; Montani and Okaichi 1985). Amino acids are, therefore, a significant fraction of the carbon flux, and can be used to estimate decomposition and process rates (Sigleo & Shultz, 1993). Changes in relative abundances of individual amino acids, as well as changes in the absolute totals, may indicate the amount or type of remineralization occurring in the water column (Lee and Cronin 1982; Montani and Okaichi 1985). Amino acids in fact have a short time scale of supply and removal and for this reason they can provide more detailed insight into specific processes, such as uptake and release by bacteria and benthic animals and adsorption on sediment particles (Henrichs and Sugai, 1993). Moreover, amino acids can influence trace elements speciation because of the formation of complexes (Ianni et al., 2000).

- ***Lipids***

Lipids are operationally defined as substances that are practically insoluble in water but extractable with non-polar organic solvents. After amino acids and carbohydrates, lipids are the next most abundant biochemical in organisms. Lipids typically account for 10-60% of organic carbon (OC) in aquatic organisms (Sargent and Henderson, 1986; Wakeham et al. 1997a,b). Lipids are important biochemicals in organisms where they play roles in energy storage and mobilization, membrane structure, and hormonal regulation of metabolic processes. They are common in naturally occurring fats, waxes, resins and essential oils.

The low water solubility of the lipids derives from their hydrocarbon-like structures which are responsible for their higher survival rates during sedimentation compared to other biogenic compound classes like amino acids or sugars. Due to their wide assortment of organic functional groups, the diverse molecular structures of lipids make them valuable "biomarkers" useful for tracing organic matter sources, alterations, transport and other biogeochemical reaction pathways (Wakeham and Lee, 1993; Sun and Wakeham, 1994). Lipids are relatively labile toward degradation in the aquatic system, potentially more reactive than amino

acids and carbohydrates (Wakeham et al., 1997a). Rapid degradation of lipid components, either by autolysis or by hydrolytic attack by enzymes from heterotrophic consumers, usually follows the death of the producer organism. Degradation results in qualitative changes in composition as the more labile compounds are lost. Lipids are rapidly degraded as particulate material moves from surface waters where it is produced to sediments where a tiny fraction of production is buried and preserved. The behavior of specific lipids is highly dependent on molecular structure, whereby short-chain compounds and highly unsaturated compounds tend to be more reactive than long-chain, unsaturated molecules. The nature of the water column and sediment bed, whether oxic or anoxic, influences the form of organic matter degradation (aerobic vs. anaerobic), and resulting differences in biochemical reaction mechanisms will influence the structure of decomposition products thus formed. Yet some structures are stable toward diagenetic reactions and are preserved in sediments, even to ancient sediments and fossil fuels. This stability provides an unambiguous link between ancient sedimentary organic matter and its contemporary biological analog, allowing geochemists to infer past oceanographic conditions (Brassell, 1993). Terrigenous, higher plant-derived compounds tend to be more efficiently preserved in sediments than are marine-derived compounds; this preferential preservation is likely related to differences in molecular structure.

- ***Phenolic compounds (Tannin and Lignin)***

The mangrove tree roots contain a large amount of tannins and the leaves contain lignins. Lignocellulose, the structural component of mangrove leaves become gradually enriched in lignin content during decomposition due to the rapid degradation of structural polysaccharide components. Simple phenolic compounds are common microbial degradation products of lignin and the occur in other substances such as tannin (Hedges 1988); both lignin & tannin are major classes of secondary products of plant metabolism and are ecologically important. However the processes involved in the decomposition of organic matter or the effects of high amounts of recalcitrant phenolic substances resulting from decomposition on the biota of the water body are not fully understood. Contrary to what has been observed in a variety of other vascular plant tissues, the lignin component of mangrove leaves is lost at approximately the same rate as the polysaccharide components (Benner et

al., 1990a). Phenolic materials are abundant in the soil and water of eutrophic environments and are the main components of soil and aquatic humic substances (Haslam 1989). They result in adverse environmental conditions such as high BOD, undesirable aesthetic effects, fish fainting or toxicity to fish and other aquatic life. The very resistant nature of lignins is suggestive of long term damaging effects on the ecosystem. Several investigations have suggested that reduction of algal productivity and biomass in brown waters could occur due to diminished light intensity and changes in light quality (Collier 1988). Tannins inhibit plant growth (Mahadevan et *al.*, 1984; Herrera and Ramirez, 1996). The effect of tannins on microorganisms and plant growth is described by Mahadevan et al., (1984). The natural phenolic materials have some negative effects on degradation activity of the microflora associated with the mangrove leaves at different stages of decomposition (Lee et al., 1990; Herrera-Silveira and Ramirez-Ramirez, 1996). Tannins significantly decrease the lipid contet in the tissues of certain fishes (Beena, 1991). The toxicity of tannins on several enzymes has been established (Gupta and Haslam, 1980). Plant-produced polyphenols entering the soil in litter or canopy throughfall may influence the pools and fluxes of inorganic and organic soil nutrients in terrestrial ecosystems. Environmental factors, such as pH, temperature, and solution polarity are known to affect chemical reactivity. Such effects could have far-ranging consequences for nutrient competition among and between plants and microbes, and for ecosystem nutrient cycling and retention. Polyphenol concentrations increase with decreasing soil fertility (Hattenschwiler &. Vitousek, 2000). In nature phenol will form complexes with nitrogenous compounds and makes them less susceptible for microbial degradation as compared to free proteins and amino acids. This reduces mineralization and release of nutrients. Therefore, the abundance of phenolics in sediment plays an important role in nutrient cycling (Joseph & Chandrika, 2000). Natural phenolic materials can influence the cycles of metals and other elements in the aquatic environment and some investigators have explained decreases in primary productivity by deficiency in Fe or other metals caused by metal complexation by dissolved humic substances (Guild fort et.al.1987; Fuller and Davis 1989). Another explanation is that when natural phenolic material react with proteins, these compounds can inhibit the performance of many enzymes (Francko, 1986; Herrera-Silveira & Ramirez-Ramirez, 1996).

Lignins play a significant role in the coal formation. As vegetable matter decomposes in water, some lignin degrades as long as oxygen is present. As the materials settles to the bottom where anaerobic conditions prevail, the cellulose portion will be decomposed via hydrolytic and fermentative reactions but the lignin portion will accumulate. The process contributes to build-up of organics in sediments and to the formation of bogs and ultimately to coal formation (Francis, 1954). The lignin component of vascular plant tissue represents a source - specific tracer that can uniquely characterize terrestrial organic matter (Hedges and Mann, 1979a, b). Hedges and co-workers (e.g., Hedges and Ertel, 1982 and Hedges et *al.*, 1984) have shown that it is possible to identify land - derived organic matter in aquatic systems, through the analysis of the oxidation products of lignin. This lignin, together with other compounds such as tannins, polyphenols and quinones can undergo condensation reactions to form the humic material that shapes a considerable part of organic material (Kononava, 1966).

- ***Humic substances***

A major fraction of the organic matter in sediments cannot be readily characterized in terms of its chemical composition. Instead, it is described by purely operational definitions based upon solubility properties. They are used to distinguish between alkali insoluble humins, and alkali soluble (extractable) humic compounds, and further more, to subdivide the humic compounds into fulvic acids, which are soluble at all pH values, and humic acids which are insoluble under acid conditions, especially where the pH is <2.0. Humic 'compounds' are not compounds in the normal chemical sense of the term because that have no fixed composition, and as they are not made up of fixed monomeric units they are 'macromolecules' rather than 'polymers' (Tyson, 1994). Because of these imprecision, there is an increasing tendency to regard this materials just 'uncharacterized organic matter', rather than using the apparently more formal label 'humic compounds'.

Humic and fulvic acids are heterogeneous and disorganized assemblages of aliphatic and aromatic compounds that together form complex high molecular weight macromolecules. The carbon skeleton of these macromolecules consists of a complex, three-dimensional network of cross-linked paraffinic structures

covalently bonded and in association with various amounts of aromatic moieties (Tyson, 1994). Their structural core is surrounded by a variety of labile hydrophilic complexes including oxygen containing functional groups such as carboxyls, phenolic and alcoholic hydroxyls, carbonyls, and also acetyl, methoxyl and amino groups (Tyson, 1994). The acid character of marine humic compounds is due mainly to carboxyl functional groups, whereas in terrestrial humic compounds it is mainly due to free and methylated phenolic functional groups (derived from lignin breakdown and amino acids) (Ertel *et al.*,1986). Compared with fulvic acids, the humic acids have considerably higher molecular weights, less oxygen-containing functional groups, and are less abundant in terrestrial organic matter and in oxic marine sediments (Rashid, 1985). An association with lipids is strongest for high molecular weight (> 100 000) humic acids (Poutanen and Morris, 1983) and may be related to the fixation of unsaturated fatty acids as aliphatic esters (Tyson, 1994). Some alkanes, pigments and fatty acids are also probably adsorbed onto the surface of the humic macromolecules (Tyson, 1994). Marine humic compounds are characterized by predominance of (highly branched) aliphatic structures, low phenol content, high sulphur content low aromaticity, relatively low molecular weights (mostly <700), lower total acidity, and higher nitrogen and hydrogen contents than terrestrial humic compounds (Tyson, 1994; Libes, 1992). Specific biochemical residues such as amino acids, sugars etc. have also been detected at the molecular level in aquatic humic substances.

Humic substances are considered as playing an important role in chemical and microbiological processes aquatic systems. However, only 10-30% of this dissolved organic substance has been characterized (Hayase & Shinozuka, 1995). Condensation reactions are said to occur within the top few metres of the sediment (Tyson, 1994). It is thought that simple compounds such as carbohydrates and proteins are condensed into complexes that are associated with hydrophobic compounds such as lipids and pigments, leading to the formation of humic and fulvic acids (Poutanen and Morris, 1983). The most common mechanism proposed for humic compounds is the 'Maillard reaction', a series of condensation reactions between reducing sugars and amines that produces melanoidins (high molecular weight, brown, acidic polymers. However, the evidence for such a mechanism occurring in nature is meagre and ambiguous (Hatcher et al., 1985); such reactions

also normally proceed at rates too slow to realistically compete with microbial consumption of the metabolizable precursors (Tyson, 1994), and the concentrations of the precursor monomeric units are also too low (Whelan and Emeis, 1992).

A common assumption in aquatic biogeochemistry is that photochemical reactivity of dissolved organic carbon (DOC) in natural waters is mainly due to the abundant humic- and fulvic acids. The high aromaticity and resulting light- and UV-absorbing properties of these compounds have been stressed as important features promoting this activity (Bertilsson & Bergh, 1999).

1.5.2 Organic carbon dynamics

- ***Mineralization***

Although real system is complex, three relatively distinct consecutive phases can be identified during breakdown of organic matter under experimental conditions (Valiela et al., 1984, 1985). These are referred to as the 'leaching phase', the 'decomposer' phase and the 'refractory phase' (Valiela et al., 1984; Kristensen, 1994). The duration and relative magnitude of each phase may primarily depend on the origin and age of the litter material, the temperature, and the redox environment (e.g. aerobic vs. anaerobic).

The leaching phase is the first change to occur in organic matter following death or senescence of the organism, and results from autolysis, the breakdown of 'cell materials' by intracellular (lysosomal) hydrolytic enzymes. Significant amounts of soluble organic compounds, mostly amino acids, mono- and disaccharides and long-chain fatty acids, are produced and then leached, resulting in the maximum rate of observed weight loss (Valiela et al., 1985). These compounds are, as a result of their dissolved state, readily available for uptake by bacteria (Benner and Hodson, 1985). Most of the leaching occurs within hours, then becomes progressively slower and is generally complete within a few days. The leaching phase is not mediated by microbes (Valiela et al., 1984).

The decomposer phase takes place after 3- 20 days following bacterial bacterial colonization of the detritus and lasts for about 0.75-2.0 years (Benner et al., 1992). The decomposer phase of degradation is significantly slower than its predecessor. The most important control on the rate of degradation during this

phase is the rate of dissolved organic matter release, which is dependent upon the hydrolytic activity of the fermenting bacteria (Nedwell et al., 1994 a, b). The rates of degradation during both leaching and decomposer phases are strongly influenced by temperature and dissolved oxygen content, and are greatest under warm and oxic conditions (Valiela et al., 1985). Degradation during the decomposer phase may be stimulated by bioturbation (Kristensen et al., 1992).

The final 'refractory' phase of degradation represents the slow breakdown of the least digestible fraction. The rate of decay during this phase does not appear to show any significant correlation with temperature, nitrogen supply, or detritus feeders (Valiela et al., 1985). Formation of refractory humic compounds and geopolymers occur during this phase (Valiela et al., 1984; Kristensen, 1994).

Mangrove sediments are extremely complex and affected by both physical and biological processes. Plants and animals interact with the sediments causing binding, bioturbation and pelletization. Physical processes such as rainfall, wind wave erosion and tidal current resuspension act as major factors contributing to mineralization (Lallier-Verges et al., 1998). Out of the microbiological processes occurring in mangrove areas, the role of fungi, algae and other macrosystems is well-recognised.

Mangrove soils are rich in organic matter, but the detritus is relatively nutrient poor and refractory resulting in low net mineralization rates (Kristensen et al., 1992, 1995). Decomposition rates of mangrove litter depend on the degree and frequency of tidal inundation, nutrient quality, climatic and edaphic factors, the presence or absence of litter- consuming fauna within forests (Robertson, 1988 and Chale, 1993; Robertson & Daniel, 1989, Kristensen et al., 1995) and substrate characteristics, such as, redox potential, temperature and moisture, climatic parameters such as precipitation, wind and solar radiation (Holmer at al., 1999) and micro-organism diversity (Hutchings and Saenger, 1987). Thus, the dynamics of litter breakdown will vary geographically. The availability of molecular oxygen (Benner et.al 1985), anatomy and intrinsic properties relating to chemical composition such as initial nitrogen and lignin contents (Benner et.al 1985,1990a) strongly influence the transformations and fate of detritus. Mangrove detritus has high C:N ratios and a significant fraction of the organic matter is considered to be refractory humic compounds and geopolymers (Benner et al., 1990; Kristensen et

al., 1994). This is probably an important cause of the observed low rates of mineralization in mangrove ecosystems despite the ambient high temperatures (Kristensen et al., 1992, 1995). Furthermore, the fragmentation and consumption of mangrove leaves by crabs may increase the decay rates by upto 2 orders of magnitude (Kristensen & Pilgaard, 1999). The interaction of organic matter (OM) with solid surfaces is an important process in the biogeochemical cycling of carbon in aquatic systems (Ding & Henrichs, 2002). Adsorption of OM to sediment particles can decrease its availability to microbial degradation (Sugai and Henrichs, 1992; Mayer, 1994; Hedges and Keil, 1995). The progressive alterations of organic matter that occur during diagenesis in the water column and sediments efficiently remove the readily identifiable organic constituents and leave behind a large fraction that cannot be characterized.

- *Aerobic vs Anaerobic (Oxic vs Anoxic)*

Aerobic decay, decay in the presence of ample free oxygen, can be symbolised as the reverse of photosynthesis. Anaerobic processes by nature are incomplete and much less efficient energetically than aerobic processes because of the inefficiency of electron transfer in either anaerobic respiration or fermentation. Anaerobic rates of mineralization of the leachable and lignocellulosic components of mangrove leaves and wood are 10-30 times lower than the respective aerobic rates. This suggests a very long residence time for mangrove detritus in anaerobic sediments (Benner & Hodson, 1985). In mangrove environments, the decay of organic matter is mainly mediated by anaerobic degradation: sulphate reduction and methanogenesis (by disproportionation). Chemoheterotrophic respiration results in the oxidation of reduced (fixed) forms of carbon. There is also a much higher energy return when this can be done in an aerobic environment. Many compartments of mangrove ecosystems, however, are anaerobic and utilize other, more available, terminal electron acceptors (i.e. NO^{-}_{3}, SO^{2-}_{4}, and even CO_2). Therefore, the availability of organic carbon and electron acceptors determine the chemical pathways that are dominating a given environment at a given time. In slightly reducing situations, nitrate is used as a terminal electron acceptor. As systems become more reducing, sulfate is used as a terminal electron acceptor. This process, called sulfate reduction, is believed to be the dominant pathway of anaerobic respiration in mangrove systems. Finally, under the most reducing

conditions, carbon dioxide is used as the terminal electron acceptor. This process, fermentation, is inhibited by sulfide production (a by-product of sulfate reduction) so it is of little importance to mangroves over a large spatial scale. Low molecular weight substrates, such as lactate, acetate, and H_2 serve as electron donors in sulphate reduction and methanogenesis, and H_2S, CO_2, H_2O and CH_4 are products.

Biogeochemical studies (Nedwell et al., 1994a,b and Kristensen et al., 1995) suggest that aerobic respiration (decomposition) and sulfate reduction (anaerobic decomposition) are the major pathways of organic matter diagenesis in mangrove sediments (Alongi et al., 1998). It was earlier thought that aerobic decomposition is much more important than anaerobic decay in mangrove sediments. More recently, it was shown that this is not always true, and that sulphate reduction may be an important electron acceptor in organic-rich deposits typical of mangrove forests (Kristensen et al., 1994; Alongi et al., 1998). A number of recent studies have revealed that the contribution of sulphate reduction varies with a number of factors such as season, benthic community activity and physical transport conditions (Kristensen et al., 2000). Sulphate reduction has been found to be responsible for upto 100% of the total benthic metabolism in highly productive and undisturbed coastal environments (Mackin and Swider, 1989), whereas values lower than 10% have been found in less productive and disturbed (currents, bioturbation and rooted plants; Kristensen et al., 1994, 2000; Banta et al., 1999) sediments.

The tidal regime has a major influence on the organic matter mineralisation. In high inter-tidal areas the sediment is only inundated for a short period during spring tides and the benthic community appears semi-terrestrial. Aerobic processes dominate due to the penetration of crab burrows and tree roots deep into the sediments (Eshky et al., 1998). Sulphate reduction may therefore be of minor importance in the mineralization of organic matter (Kristensen et al., 1995; Holmer et al., 1999). The duration of inundation is longer in low intertidal mangrove forest areas. The benthic community is of more marine origin, but faunal diversity and abundance are low in the unpredictable environment. Surface sediments are usually oxidized, but due to the sparse benthic fauna, anaerobic processes may dominate mineralization in the deeper layers with sulphate reduction being responsible for more than half of the total benthic metabolism (Kristensen et al., 1992, 1995; Holmer et al., 1999).

- *Export vs Import*

Mangrove swamps export mangrove litter and this enhances bacterial productivity in adjacent coastal waters (Alongi et al., 1989). The extent of outwelling is related to the geomorphology of the tidal basin, tidal amplitude and water motion, and the ratio of the areal extent of the vegetation to the receiving open ocean area (Alongi, 1990a,b).

However, the information available on this phenomenon is confined to few regions in the world and often controversially (Dittmar & Lara, 2001a,c). Adjacent mangrove areas in Hinchinbrook Island (Australia) were source and also effective sink for dissolved nutrients and organic carbon (Alongi, 1996; Alongi et al., 1998; Ayukai et al., 1998). Twilley (1985) determined net-export of dissolved and suspended organic carbon from mangroves in Rookery Bay (Florida, U.S.A.). Wattayakorn et al. (1990) reported outwelling of inorganic nutrients from mangroves in Klong Ngao (Thailand). In Terminos Lagoon (Mexico), the mangrove seems to be rather an importing system for dissolved nitrogen species (Rivera Monroy et al., 1995). Simpson et al. (1997) found an almost balanced net exchange for nitrate between Malaysian mangroves and adjacent coastal waters, whereas other inorganic nutrients showed large variability in their fluxes. In Braganca (North Brazil), strong outwelling of nutrients and organic matter was measured, exceeding that of other mangroves in the world (Dittmar & Lara, 2001a,c). The reasons for this large variability are hitherto poorly understood. Ayukai et al. (1998) found differences between two adjacent mangroves with different freshwater inputs, and put forward variations in tidal-range, topography, sediment chemistry or community structure as other possible reasons for the inconsistencies among export balances.

The export of organic matter, like primary productivity, seems to be dependent upon the hydrologic characteristics. It is important to note, however, that not all mangrove systems are net exporters of organic carbon. Systems that have little or no hydrologic energy may be net importers of organic carbon.

1.6 METALS IN MANGROVE SEDIMENTS

Anthropogenic activity has introduced significant amount of heavy metals into aquatic environment in a non-conservative manner (Bethoux et al., 1990; Campbell et al., 1988). The behaviour of these elements in the aquatic system must be addressed, both to assess and understand the nature and extent of man's influence, and because most of them are potentially toxic.

The coastal habitats of Kochi is deteriorating rapidly due to urbanization, recreational development, and industrial installations which are now underway near many of the mangrove areas, representing a direct threat to these forests. In order to protect and conserve these fragile mangrove ecosystems, this study which would help in the preservation of biodiversity of this area was undertaken to investigate the potential of their alteration by existing inputs from anthropogenic waste disposal and other activities. Pollutants like oil, solid wastes and industrial wastes reaching mangrove environments can cause damage to mangrove roots that may affect the respiratory and osmoregulatory capabilities of the plant leading to death (Getter et al., 1981) and/or exert acute and chronic effects on aquatic organisms. Among pollutants, heavy metals have been of interest because of their toxicity, persistence, and prevalence on the environment (Cosma et al., 1979).

Analysis of pollutants in sediments has become an important tool for tracing anthropogenic pollution of water (Senten, 1989), because some pollutants are adsorbed by material in suspension and by fine-grained particles. After flocculation and sedimentation they are enriched in bottom deposits by a factor of 1000 or more (Forstner, 1979). The present study attempts to provide the first baseline information concerning the levels of numerous heavy metals in surface and core sediments of three-selected mangrove ecosystems of Kochi.

1.7 SCOPE OF THE PRESENT STUDY

A perusal of available literature indicates that work done hitherto on coastal habitats, particularly mangrove ecosystems in Kerala focus predominantly on biological and geological aspects. No significant attempt for a systematic chemical investigation on mangrove ecosystem in Kerala has been reported.

Mangrove environment is an aquatic zone capable of trapping large quantity of pollutants, particular heavy metals, nutrients, organics etc. Mangrove forest sediments can provide a sink for these materials that are derived from marine and terrestrial sources. Direct adsorption, complexation with organic matter and the formation of insoluble sulphides all contribute to the trapping mechanism. The concentration and chemical speciation of these materials are influenced by the distribution of geochemically distinct zones within the sediment. A major part of organic matter in natural waters and sediments is composed of amino acids, proteins, carbohydrates, lipids, phenolic compounds, humic substances, etc. Most of these substances are derived from decaying vegetation and play a significant role in the productivity and biological cycle in the aquatic environment, either inhibitory or stimulatory. The type of flora in the watershed, the distribution and abundance of wetland and littoral plants, and the pathways of release of detrital organic material into the water body have different effects on overall rates of eutrophication and development of aquatic ecosystem. There is little information on the chemical import of these compounds vis-à-vis the sustainable development of estuarine / wetland habitats. Rigorous, long term studies on biogeochemical status, temperature, pH, oxygen content, alkalinity, salinity, soil texture, etc., it is hoped, would be required to generate a holistic appreciation of the biogeochemical interactions that regulate the mangrove environment. Therefore, it was considered desirable to attempt a characterization of these compounds with a view to ascertaining their role in effective management of this ecosystem. It is possible that some of the above mentioned compounds could be used as biomarkers, by means of which, the origin and transport of organic matter across a water system can be evaluated. The present study aims at investigating variations, the relative proportion of dissolved, particulate and sedimentary fractions of these materials, as well as nutritional quality and the pollution extent so as to be able to comment on the role of wetland ecosystems, particularly with regard to their contribution to coastal nutrient budget, food chain, and hydrochemistry etc. This study, it is hoped, will not only increase the knowledge on the stability and resilience of coastal ecotones subjected to natural or anthropogenic perturbations but will also contribute to the generation of scientifically-based information on coastal management and protection.

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Chapter 2

MATERIALS AND METHODS

2.1 DESCRIPTION OF THE STUDY AREA

Water samples, particulate matter and both surface and core sediments we collected from the three mangrove regions of Kochi, during the period from Ap 1999 to December 2000 at monthly intervals. The sampling sites are shown in t Fig. 2.1. 'Station 1', Murikkumpadam is a densely populated area with the dwellir units of fisherman and other poor people encroaching on the mangrove areas. T discharge of sewage and disposal of garbage and solid waste add to the problem pollution. 'Station 2', Puthuvyppu, is a mangrove nursery of fisheries station insi the campus of Kerala Agricultural University and is free from sewage inputs. Static 1 and Station 2 forms the major part of island called 'Vypin' and lie almost adjace to each other 'Station 3', Aroor is a dwindling mangrove site with low plant densit To compare the parameters under study with that of a non-mangrove site, sampl were collected from an estuarine reference station (Station R) also.

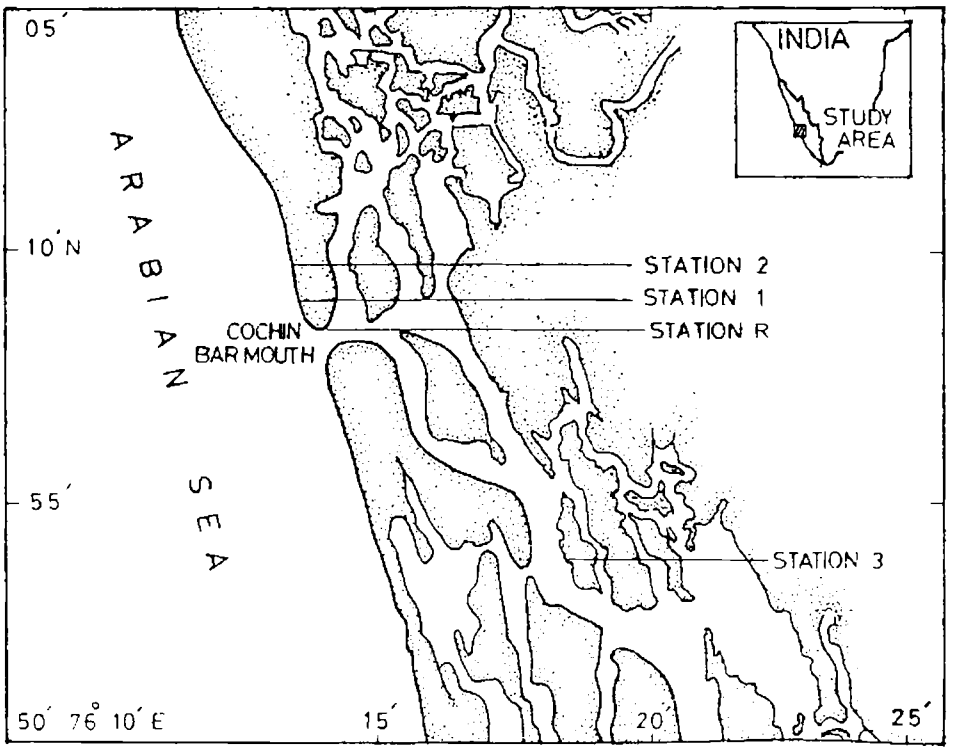

Fig. 2.1 Map of Cochin estuary showing location of sampling sites

2.2 SAMPLING AND STORAGE

Collection of Water Samples

All collecting scoops, bags and containers were acid washed and rinsed thoroughly with Milli-Q water before use. Surface water samples were collected from each station using a thoroughly cleaned acid-washed plastic bucket. The samples were then transferred carefully to pre-cleaned polythene bottles. General hydrographical parameters were measured immediately after the sampling. pH measurements were made immediately after sampling using a portable pH-meter. The temperature was measured using a sensitive thermometer designed to read upto 0.05°C. The samples for determining dissolved oxygen were collected in 50ml DO bottles and were fixed in situ, using 'Winkler A' and 'Winkler B' reagents and those for alkalinity (25ml) were taken in a bottle containing 10ml of 0.01N HCl.

Collection of Sediment Samples

Surface sediment samples (approximately 1 kg) were collected from each station except Station R, using a plastic scoop in labeled plastic bags. A 30-cm sediment core was also collected close to the vegetation, without cutting roots and rhizomes to prevent leakage of root exudates. Only cores with a minimum of benthic animals were chosen to limit the effect of fauna on the sediment processes. Sometimes it was not possible to collect cores of this length, but shorter ones were sampled. Immediately following retrieval, the core was sectioned at 0-2, 2-4, 4-6, 6-10, 10-20 & 20-30 cm intervals, slices from the same depth were combined and subsections were stored frozen in plastic bags until analyzed in a refrigerator. Samples were transferred to the laboratory on crushed ice and stored frozen to minimize changes. In the laboratory, samples were defrosted, air dried without previous washing and then finally pulverized using an agate mortar.

A diurnal collection was also conducted out of curiosity to study the tidal influence on organic matter content. For this the water samples were collected at 1100hrs, 1300hrs, 1600hrs, 2100hrs, 2300hrs, 200hrs, 400hrs, 800hrs and 1000hrs in accordance with tidal levels on 11th and 12th of February, 2000 from Station 1, Station 2 and Station R. Station 3 was omitted as it was some what far away from the other three.

2.3 FILTRATION FOR DISSOLVED ORGANIC MATTER AND PARTICULATE ORGANIC MATTER (POM)

Particulate matter was separated from dissolved fraction using GF/C filter having 0.45 µm pores and 47mm diameter. Filters were preheated in a muffle furnace at temperature range 450°C 500°C for 2hrs. (Strickland and Parsons, 1972). These filters containing POM were stored in a petridish and kept in a deep freezer. The filtered water samples were kept at 0°C to minimize changes due to storage.

2.4 ANALYTICAL METHODS

All glassware and plastic ware were thoroughly cleaned with acid and then with Milli-Q water. All reagents were of analytical grade. Reagent solutions and standard solutions were prepared in Milli-Q water. Methods employed for each of the analysis were as follows:

2.4.1 Physico-Chemical Parameters

The physico-chemical parameters like pH, Temperature, Salinity, Dissolved Oxygen, Alkalinity, Hardness, Total Suspended Solids and Chlorophyll were estimated by standard procedures.

- *Salinity*

Salinity of the water sample was determined on the same day of collection by Mohr-Knudsen titrimetric method [Grasshoff et al., 1983)].

- *Dissolved Oxygen*

Dissolved oxygen was fixed immediately after collection and then determined chemically using Winkler's Method (Grasshoff et al., 1983).

- *Alkalinity*

Alkalinity was determined by adding a fixed amount of 0.01N HCl to the sample immediately after sampling. It is then titrated with standard 0.01N NaOH using bromothymol blue as indicator (Grasshoff et al., 1999).

➢ *Hardness*

Hardness was determined by EDTA titration method using Eriochrome Black-T as indicator (APHA, 1985).

➢ *Chlorophylls*

The pigments are extracted from particulate matter with aqueous acetone and their concentration is determined spectrophotometrically (APHA, 1985).

2.4.2 Estimation of Organic compounds

➢ *Sedimentary Organic Carbon (SOC)*

SOC was determined by employing wet oxidation method [El Wakeel and Riley Method, 1957; Gaudette and Flight, 1975] which involved the oxidation of organic matter present in the sample by a known quantity of chromic acid. The amount of the acid consumed was determined by back titration with 0.5 N ferrous ammonium sulphate (Mohr's salt) solution using ferroin as indicator. The end point was the colour change from green to red.

➢ *Particulate Organic Carbon (POC)*

Estimation of POC was by the method of oxidation of organic matter present in the GF/C filter paper (Strickland and Parsons, 1979). Filter paper containing particulate matter was placed in beaker containing 1ml 70% phosphoric acid and 1ml Milli-Q water. Suitable volume of sulphuric acid – dichromate oxidant was added and placed again in a water bath for about 15 minutes more. After cooling 10ml of water was added and titrated against standardized 0.25N ferrous ammonium sulphate (FAS) solution using ferroin indicator until the colour changed from green to red.

➢ *Sedimentary Organic Nitrogen*

Total nitrogen in the sediment was estimated by a modified Kjeldhal method (de Lange, 1992). To 1 g of dried, finely ground sample added 6ml of conc. Sulphuric acid, and mix katalyser (Merck) were added; after regular mixing solution was gently boiled for half an hour. The colour of the solution changes to white greenish. The solution centrifuged and the clear centrifugate and washings were transferred to a sample holder connected to the steam distillation unit. 25ml of

10 N KOH was added and the ammonium was distilled into 25ml 1% boric acid t which 5 drops of mix-indicator A (Merck) were added. The distilled ammoniun was determined by back titration with 0.1N hydrochloric acid.

- *Carbohydrates*

Carbohydrates were estimated by the phenol-sulphuric acid method (Dubo et. al., 1956). To 1ml of the sample, 1 ml of 5% phenol and 5 ml of Conc.H_2SO were added. After cooling the test tube at room temperature, absorbance wa measured spectrophotometrically at 490 nm using a Hitachi (model no:- 150-20) UV Visible Spectrophotometer. Blank and standards of D-glucose were also treate similarly. Blank corrections were applied to all set of readings. A calibration curv was plotted from which the concentration of dissolved monosaccharides wa obtained. To obtain the total dissolved carbohydrates, the samples were hydrolyze with 1 N H_2SO_4 in a 1:1 ratio at 100°C for 1 hour and measuring the absorbance aft developing the colour using phenol and sulphuric acid. Total carbohydrates from th sediment and particulate samples were leached with 1N H_2SO_4 at 100°C for 1 hour Cooled and filtered the samples and aliquots were taken in clean test tubes an measuring the absorbance after developing the colour. Monosaccharides wer determined without sample hydrolysis. Polysaccharides concentrations wer estimated by subtracting the concentration of Monosaccharide from concentrations o total carbohydrates (Burney and Sieburth 1977).

- *Amino acids*

Free amino acid was determined by fluorescence method (Parsons et al 1984) using o-phthalaldehyde, which in presence of 2-mercaptoethanol, reacts wit primary amines form highly fluorescent products. 1ml of the sample (1ml of th extract after leaching with Milli-Q water for sediments and particulate matter an 1ml of the sample as a whole for water) was treated with 5 ml of buffered O phthalaldehyde reagent (1ml of 2-mercaptoethanol was added to 400ml of borat buffer, to which 20ml of 10% o-phthalaldehyde solution in 95% ethanol was adde and used after 1hr), and measuring the fluorescence at excitation wavelength o 430 nm and emission wavelength of 540nm, in a fluorescence spectrophotomet (Hitachi F-3010 Fluorescence Spectrophotometer). Blank values were subtracte

from sample readings and concentration of free amino acids were obtained after plotting a calibration curve using glycine as standard.

Concentration of combined amino acids are typically estimated by measuring amino acid concentration released after vapor phase hydrolysis as suggested by Tsugita et al., (1987). Samples were dried under a stream of nitrogen gas in muffled 1-ml test-tubes. The test-tubes were inserted into wide mouth 10-ml glass vials containing the acid mixture (0.175ml of 7N HCl, 10% trifluoroacetic acid (TFA), 0.1% phenol; the vials are sealed after flushing for 5 min with nitrogen gas. Samples were hydrolysed in the vapor phase at 156°C for 23 min. After hydrolysis and cooling, samples were dried under a stream of nitrogen gas to remove any acid, and then analysed for aminoacid concentrations by o-phthalaldehyde. The concentration of free amino acids was subtracted from concentrations determined after hydrolysis to give estimates of Combined amino acids.

➢ *Proteins*

Proteins in dissolved phase was measured using copper reagent and Folin-Ciocalteu phenol reagent (Lowry et al., 1951). The method adopted was as follows: the samples were treated with 1N NaOH at 80°C for 30 minutes to dissolve the proteins. After cooling and centrifuging, 1ml of the extract was transferred to clean test tubes and 5ml of copper reagent (mixture of 2ml each of 2% $CuSO_4$ and 4% Sodium potassium tartarate and 96ml of 3% Na_2CO_3 in 0.1 N NaOH) were added followed by 0.5ml of Folin- Ciocalteu phenol reagent (1:1 mixture) after 10 minutes. After 40 minutes, samples were analysed spectrophotometrically at 750nm against reagent blank. A calibration curve using Bovine albumin was plotted from which the concentration of proteins in the samples was obtained.

➢ *Total lipids*

Estimation of total lipid was done by the Sulphophosphovanillin method suggested by Barnes and Blackstock (1973). To 10 ml of the sample, 10ml of chloroform-methanol (2:1v/v) mixture and 20 ml of 0.9% (w/v) aqueous NaCl were added in a separating flask and after thorough shaking, the preparation was allowed to stand for 30 minutes. From the clean biphasic layer formed, the lower phase was removed and the same quantity of chloroform was added to make up the volume. This extract was dried in a vacuum desicator, over silica gel and added 0.5

ml conc.H_2SO_4, boiled maintaining in a water bath at 60°C. After cooling to roo temperature 5 ml of vanillin reagent (0.2% vanillin in 80% (v/v) orthophospho acid) was added and allowed to stand for 30 minutes. The absorbency of the pi colour developed was measured at 520 nm using spectrophotometer. A standa was also run employing the same method using cholesterol. Blank solution was ml of chloroform-methanol mixture.

Lipids were extracted from the sediments and particulate matter according the method of Bligh and Dyer (1959). A known amount of the sample is extract with 2:1 (v/v) mixture of chloroform and methanol. The extraction was extract four times. The extracts were pooled together and dried in a vacuum desicator, ov silica gel and developed the colour using conc.H_2SO_4 and vanillin reagent.

➢ *Tannin and Lignin*

The estimation of dissolved Tannin & Lignin was performed by the sodiu tungstate-phosphomolybdate acid method method (APHA, 1995). The princip involved is the determination of a blue colour on reduction of Folin-Ciocalt phenol reagent by the aromatic hydroxyl groups present in tannins and lignins. Tl effects of Mg and Ca hydroxides and/or bicarbonates present in the sample we suppressed by the addition of trisodium citrate solution (Nair et al., 1989). To 10 of the sample, added in rapid succession 5ml of 1.6M tri-sodium citrate solut followed by 1ml of Folin-Ciocalteu phenol reagent and 10ml of carbonate-tartara reagent (200g Na_2CO_3 and 12 g sodium carbonate in 750 ml hot distilled wat cooled to 20°C, and dilute to 1litre) and allowed to stand for 30minutes for colo development. Reagent blanks were similarly prepared omitting the sample. Tl absorbance was measured spectrophotometrically at 760nm against blank. Tl concentrations of each samples were calculated from the calibration curve obtain using tannic acid standards.

Sediments and particulate matter were subjected to 0.05M NaOH leachi for 72 hours and sub sampled at 5, 15, 45 and 120 minutes and thereafter at rando upto 72 hours. The sediment to solution ratio was maintained at 500mg: 250m 5ml of the supernatant liquid was withdrawn for analysis as described for wat samples. The blank solution was 0.05 NaOH.

➢ *Humic substances*

The extraction of humic acid was done by the used for the extraction of IHSS soil humic acids (Swift, 1993). A known quantity of the dried sediment and particulate matter (air dried at room temperature and then at 60°C for 6hours) was extracted with 1N NaOH for 24 hours, filtered and the fluorescence was measured at excitation wavelength of 362nm and emission wavelength of 462nm in a Hitachi F-3010 Fluorescence Spectrophotometer. Humic acid standard was prepared by dissolving purified humic acid, which was isolated from mangrove sediments as follows: Mangrove sediments were taken in 2 litre beakers and treated with 0.5N NaOH for 24 hour with occasional stirring. The mixture was then filtered. On acidification of the alkali extract with 6N HCl, humic acid was precipitated, which was purified by employing repeated base-dissolution, acid-precipitation cycles. Finally, humic acid was suspended in dilute HCl-HF mixture (5ml HF + 5ml HCl + 990ml distilled water) to eliminate weak base insoluble materials, as suggested by Khan (1971). Humic acid was separated, washed with Milli-Q water and dialysed (Cellophane paper) against Milli-Q water for five to seven days. The purified humic acid thus obtained is then dried in oven below 60°C and was kept in desicator. Dissolved humic substances were estimated by directly measuring the fluorescence.

➢ *Trace metals*

A known weight of the sediment samples were digested in a 1:1:3 mixture of perchloric acid, nitric acid and hydrochloric acid at 60°C on a hot plate until the residue turned white. The residue was washed with a minimum amount of Milli-Q water, centrifuged and decanted the clear solution, which was then made upto 50ml. Sediment-free blanks for heavy metals were also prepared in triplicate, using the same standard procedure as that for the samples. The amount of the metals (Cu, Ni, Zn, Co, Pb, Cr, Mn, Fe) present were directly determined by AAS directly aspirating the sample into the air-acetylene flame and that of Ca, Na and K by flame photometer [APHA, 1985].

➢ *Texture Analysis*

Texture analysis was conducted based on Stoke's law, which states that the settling velocity of fine sized particles is directly proportional to the size or the

diameter of the particles. The procedure was as follows: After removing carbonate by adding 10% HCl the sediment samples were treated with hydrogen peroxide for removing organic matter. A known amount of sediment collected by filtering was used for the texture analysis, which was carried out by sieving and pippetting method. A known weight of wet sediment was dispersed overnight in .025N sodium hexameta phosphate (Calgon) solution. The sand fraction was separated from the dispersed sediments by wet sieving using a 230 mesh (63μm) ASTM sieve (Carvar, 1971). The filtrate containing silt and clay fraction was subjected to pipette analysis (Krumbein and Pettijohn, 1938: Lewis 1984).

2.5 STATISTICAL ANALYSIS

The monthly data on various constituents are reduced to seasonal averages of premonsoon (February - May), monsoon (June - September) and postmonsoon (October - January) in order to establish a reliable trends. Monthly and seasonal variation tables are given in Appendix A. Differences in parameters with station and season were tested using two-way (site x season) ANOVA and that with station, season and depth in core sediments by three way (site x season x depth) ANOVA, the results of which are given in Appendix B. Correlation analysis was carried out to find out inter-relation among different parameters and the correlation coefficients are given in Appendix C.

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Chapter 3

HYDROGRAPHICAL PARAMETERS

A detailed study of the variations in parameters such as temperature, salinity, dissolved oxygen, pH was also carried out along with the organic matter analysis of mangrove environment. The significant changes in these chemical constituents are brought about by variations in hydrographic features associated with the SW monsoon. It has long been established that the concentrations of many components in the aquatic system are controlled by factors like salinity, pH and other major and minor ionic concentrations. Hence the study of these parameters is indeed quite relevant in the present context. The results of the present investigations are presented and discussed in the following sections.

A diurnal study was conducted to assess the changes, if any, that occurred with time or tidal levels. However, results of this study indicated that there was no significant variation of parameters with time or tide as confirmed by ANOVA (Table B.2). Therefore, sampling strategies were designed and carried out irrespective of tidal variation.

3.1 Temperature

Temperature of the environment is a major and even the deciding environmental factor in determining growth rate, metabolism, and nutritional efficiency of aquatic life. In fact, temperature will influence all biological and chemical processes in an aquatic system.

The data regarding temperature distribution for the 4 stations is given in the Table (A.1). Seasonal and diurnal variations are shown in Fig. 3.1a and 3.1b respectively.

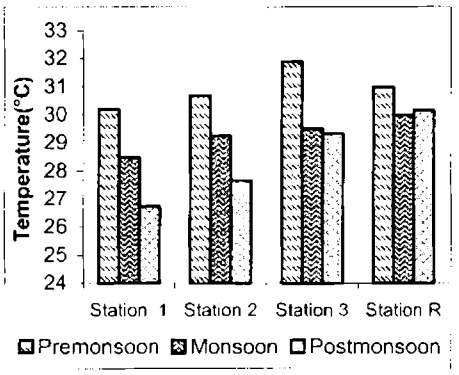

Figure 3.1a:- Spatial and seasonal variation of temperature

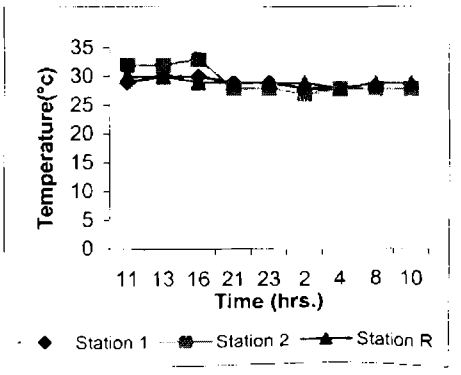

Figure 3.1b:- Spatial and diurnal variation of temperature

Monthly data showed the maximum temperature (35°C) in the month of April'99, at Station 3 and the minimum (21°C) in October'00 at Station 1. At all the four Stations, the highest temperatures were observed during pre-monsoon and the lowest during postmonsoon. In all the seasons, except during premonsoon, Station R exhibited high temperature. Temperature decreased in the order, Station R > Station 3 > Station 2 > Station 1 during monsoon and postmonsoon, but during premonsoon, the trend was, Station 3 > Station R > Station 2 > Station 1. ANOVA showed significant variations between stations and seasons (Table B.1).

The temperature variation in the present study was predominantly diurnal with a mean value of 29.07°C. The maximum temperature (27°C) was observed at 1600hrs at Station 2 and the minimum (33°C) at 200 hrs. in the night at Station 2 itself. Therefore, the temperature variation was mostly observed at Station 2.

3.2 pH

pH is another important parameter which exerts definite influence on speciation of elements in water. The solubility of different constituents is dependent on pH. The pH also controls the growth of organisms regulating the activity of enzymes. In open ocean waters, pH ranges between 7.8 and 8.4. Variation in pH of coastal waters is caused by many factors. Aquatic pH generally vary from 7.0 to 7.5 in the fresher sections, to between 8.0 and 8.6 in the more saline areas. The slightly alkaline pH of seawater is due to the natural buffering from carbonate and bicarbonate dissolved in the water. During monsoon season, the fresh water discharge from the rivers lowers the pH. Photosynthesis, denitrification and sulphate reduction increase pH, whereas processes such as respiration and nitrification decrease pH (Zhang, 2000). When photosynthetic reactions take place in the aquatic system, CO_2 is reduced to carbohydrate. Thus the higher pH values for surface waters are caused by the enhanced photosynthetic activity occurring at the surface. Respiration and degradation/ decomposition of organic material are the reactions that proceed in the opposite direction of the photosynthesis. Oxidation of organic matter leads to increase in CO_2 levels and to a shift of equilibrium to the lower pH. Other factors that determine the pH of the water include bacterial activity; water turbulence; chemical constituents in runoff flowing; sewage outflows; and impacts from other anthropogenic activities.

Changes in pH can alter other aspects of the water chemistry, usually to the detriment of native species. Even small shifts can affect the solubility of some metals such as iron and copper. It has been shown that a pH of 1.5 or less was necessary to ensure that the entire metal ion remained in solution. Speciation of elements undergo considerable changes in the pH range of 7.5 to 8.5. Lowering of pH levels could trigger the resuspension of toxic metals from the sediments into the water column and this can seriously impact many aquatic species.

Values of pH at various stations during the present investigations are given in the Table A.2. Seasonal and diurnal variations are depicted in the Fig. 3.2a and 3.2b respectively.

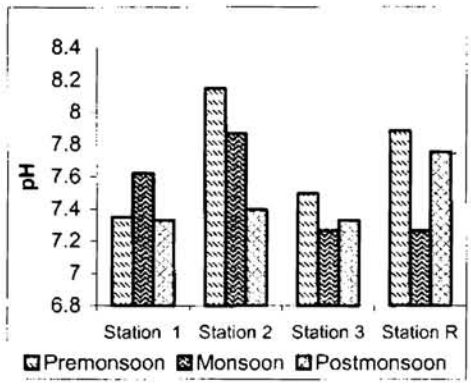

Figure 3.2a:- Spatial and seasonal variation of pH

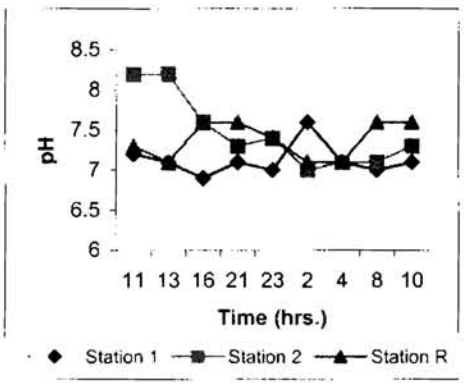

Figure 3.2b:- Spatial and diurnal variation of pH

Monthly variation of pH was in the range 6.8 to 8.8 with an overall mean value of 7.56. pH was directly correlated to DO (Table C.1a-d) at Station 1. This may be due to increased photosynthesis at this Station. Water bodies with high alkalinity have high pH values while those with low alkalinity have low pH values. Station 2 showed a range from 6.9 to 8.8 with a mean value of 7.81, at Station 2, the pH is positively related to DO. At Station R the range was from 6.94 to 8.42 mean value being 7.64. At Station 3, the range was 6.8 to 7.93, with a mean value 7.36. At Station R a highly significant positive correlation was found between pH and hardness. The overall seasonal range showed the highest at Station 2 during premonsoon and the lowest during monsoon at Station 3 and Station R. The high correlation between pH and hardness was found during monsoon season also (Table C.2b).

In the diurnal study, pH ranged from 6.9 (at 1600hrs. at Station 1) to 8.2 (1100hrs. and 1300hrs. at Station 2). Except at 200hrs. Station 1 showed the lowest pH values. This might be due to the decomposition of organic matter in sewage overflow from the nearby-inhabited area. Diurnal data showed a direct relationship of pH with salinity and inverse relationship with POC at Station 1. pH decreases with increase of organic matter load. At Station 2 pH was determined by temperature, DO and alkalinity. Station R showed no significant correlation.

The lower pH values of mangrove areas were mainly due to the microbial degradation of organic materials such as mangrove detritus, which depletes oxygen and makes way for bacterial sulphate reduction (Berner, 1983) leading to the production of hydrogen sulphide. Samples collected from mangrove areas especially those of Stations 1 and 2 were often anoxic and had a pronounced odour of hydrogen sulphide. The reduction in pH values during postmonsoon at Stations 1 and 2 and during monsoon at Stations 3 and R was due to the effect of precipitation. Acidic mangrove deposits may be the result of several processes, including oxidation of reduced compounds (NH_3, H_2S, FeS_2) or the dominance of aerobic decomposition of organic matter which results in the net production of carbonic acid (Middelburg et al., 1996; Alongi et al., 1998). The activities of *Rhizophora apiculata* are known to lower the pH and alkalinity of sediments (Kristensen et al., 1991). Another acid-generating mechanism may be the leaching of polyphenolic acids from the standing amounts of leaf litter and slash lying on, and buried in, these water and sediments. Polyphenolic acids are a major component of pore-water dissolved organic carbon (DOC) pools (Boto et al., 1989) and DOC leaching from mangrove leaves (Benner and Hodson, 1985).

3.3 Salinity

Of all the hydrographic parameters, salinity is perhaps the most important one being an index of the amount of dissolved solids in water. Salinity varies with depth and from place to place. The principal natural processes, which lead to, changes in the salinity are those, which bring about the removal or addition of freshwater. Increase in salinity is caused by evaporation and by the removal of almost pure water, as ice, during freezing. Decrease in salinity results from atmospheric precipitation, run-off from land, tidal intrusion etc.

The results obtained in the present study are tabulated in the (Table A.3). Monthly data showed the maximum salinity 31.86‰ in the month of May at Station 2 and a minimum of zero in the month of August'99 at Station 3. Mean values of Stations 1, 2, 3 and R were 15.98‰, 17.38‰, 9.33‰ and 11.26‰ respectively. Salinity was minimum in July and October, which reflected the active periods of south west and north east monsoons respectively. High values of salinity at mangrove sites may be due to high rate of the evapotranspiration (Dittmar and Lara, 2001) which precipitates more and more salts with each incoming tide.

At all the four stations salinity was maximum during premonsoon (Fig 3.3a). Station 3 showed the lowest salinity in all the three seasons. Seasonal data showed the highest salinity at Station 2 during premonsoon and the lowest was observed at Station 3 during monsoon. Overall mean value obtained was 13.38‰. The salinity at the Station 3 was comparatively lower while that at the other two mangrove sites were more or less the similar. The lower value of salinity at this station may be due to freshwater discharge. ANOVA showed significant difference between stations and seasons (Table B.1).

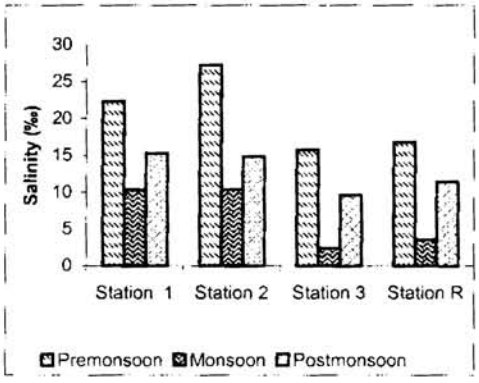

Figure 3.3a:- Spatial and seasonal variation of salinity

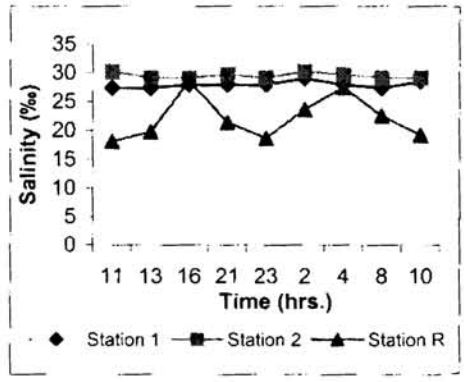

Figure 3.3b:- Spatial and diurnal variation of salinity

Diurnal variation of salinity of the mangrove sites was almost parallel (**Fig 3.3b**). Both mangrove stations showed higher salinities compared to the Station R, with the highest being recorded at Station 2, the maximum (30.26‰) being at 1100hrs. The lowest salinity (18.16‰) was also found at 1100hrs. at Station R. All Stations except Station R showed only slight changes in salinity. The tidal effect was more pronounced at Station R. Effect of tide was not a significant factor at

mangrove stations probably because of the complex network of roots, pneumatophores, creeks and channels, which restricted the free flow of water.

The mean salinity was controlled by evaporation and transpiration by mangroves. Seasonal variability of salinity was significant. During pre-monsoon salinity increased due to evaporation and low discharge of freshwater. The evaporation rate may be the highest during pre-monsoon with low or no rainfall, which explain the highest values of salinity during this period. The extreme drop in salinity to near freshwater conditions observed during monsoon at Station 3 was resulted from the considerable dilution due to the heavy influx of freshwater. Salinity was higher in May which was attributed to the combined effect of high insulation, evaporation and cessation of freshwater and/or high saline water influx due to the absence of rainfall. Lower salinity in August may be due to high freshwater influx coupled with intense rainfall during monsoon especially at Station 3. Thus, freshwater input and tidal fluctuation determine salinity distribution at Station 3, whereas monsoonal and postmonsoonal precipitation reflects the salinity variation at Station 1 and Station 2.

Salinity showed positive relationship with hardness at all stations (Table C.1a-d). This may due to the fact that Ca and Mg which contribute to hardness, contributes to salinity also. Thus, Ca and Mg behave in a conservative manner at all the four Stations. Salinity showed a direct relationship with TSS and alkalinity during premonsoon, and an inverse relation with DO during monsoon (Table C.2a-c). It is well known that the salt content of water reduces the solubility of gases and that therefore, the concentration of DO is regulated by the salinity. This implies that freshwater inputs may enhance productivity and increase levels of DO.

Diurnal correlation data (Table C.3a-c) showed a direct relationship between salinity and pH and an inverse relationship with DO at Station 1. At Station R, salinity showed an inverse relationship with temperature, which may due to increase of salt content by evaporation.

3.4 Dissolved oxygen

Dissolved oxygen (DO) plays a vital role in the aquatic environment being essential to the survival of aquatic life. Oxygen enters the water primarily through

direct diffusion at the air-water interface and through aquatic plant photosynthesis. The quantity of oxygen dissolved in water is determined by a number of factors such as temperature, salinity, partial pressure of the gas in the atmosphere, biogeochemical processes like oxidation and reduction, biochemical degradation of organic matter, respiration, photosynthesis, biological activity, currents and mixing processes etc. In fact, the maximum amount of oxygen that can be dissolved in water is only about 8.3 mg/l at standard temperature and pressure and is referred to as oxygen saturation, which is influenced by temperature, elevation (tidal level), and salinity levels.

The competing processes of photosynthesis and respiration are the main causes of in situ changes in the concentrations of dissolved oxygen and carbondioxide in the water. Photosynthesis by phytoplankton leads to the removal of carbondioxide and to the liberation of oxygen. Dissolved oxygen is consumed by the respiration of plants, animals and bacteria. The ultimate factor limiting the consumption of oxygen is the supply of organic matter. Microbial degradation of the high content of organic matter in mangrove areas generally removes all oxygen from water creating anoxic conditions with a pronounced smell of hydrogen sulphide. Because the oxygen is involved both in the photosynthetic and degradation processes in nature, oxygen is not a conservative element in the natural waters.

In the present study, DO showed monthly variations at all the four stations with a maximum (9.66ml/l) in April'99 at Station 2 and a minimum (0.224ml/l) in November'00 at Station R (Table A.4). Annual mean values at each station were 2.60ml/l, 3.60ml/l, 3.96ml/l and 3.50ml/l for Stations 1, 2, 3 and R respectively with an overall mean value of 3.52ml/l was obtained. DO also showed a seasonal variation with exceptionally very high (6.35ml/l) during premonsoon at Station 2 (Fig. 3.4a). Postmonsoon showed the lowest DO values at all the four stations and the minimum was obtained at Station 2 during postmonsoon, which may be due to low primary production or high rate of decomposition. ANOVA (Table B.1) showed significant fluctuation between stations and seasons.

In a similar study by Sheeba et al.,(1996) DO ranged between 2.00 and 8.75ml/l respectively for Puduvypeen and Nettoor.

DO showed a positive correlation with pH (Table C.1a-d) at Station 1 and with temperature and pH at Station 2. Increase of DO with temperature may be related to increase in light intensity, which increases the rate of photosynthesis. Also warmer temperature increases the rate of photosynthesis. During monsoon DO showed negative relationship with salinity (Table C.2b). Inverse correlation was found between salinity and DO implying that freshwater inputs may enhance productivity and increase levels of DO. The amount of dissolved oxygen depends upon salinity and indicates inverse relation with high salinity water showing low DO.

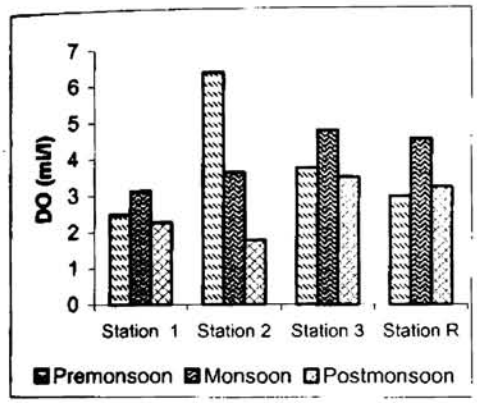

Figure 3.4a:- Spatial and seasonal variation of dissolved oxygen

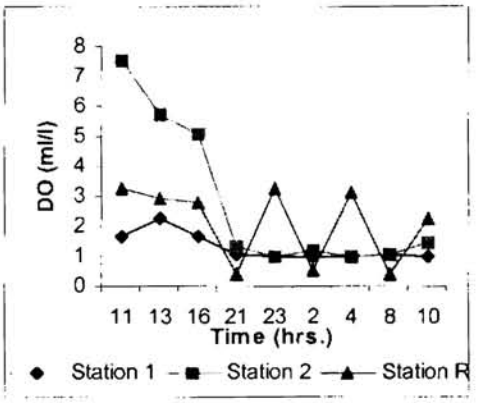

Figure 3.4b:- Spatial and diurnal variation of dissolved oxygen

In the diurnal study, DO showed variation from a minimum of 0.413ml/l (Station 3, 2100hrs and 800hrs.) to a maximum of 2.3ml/l (Station 2, 1100hrs.) with an overall mean value of 2.079 (Fig. 3.4b). In general, all the lower values were observed at night except for reference site. It may be due to the fact that at night, surplus organic matter degradation depletes most of the DO from water. During daytime, photosynthesis counterbalances respiration and organic matter degradation, whereas at night although respiration and degradation continue, photosynthesis ceases with no DO production at all which account for the low value of DO at night. Station R exhibited a lower DO range. This could be attributed to lower productivity at this site compared to mangrove sites. But after dawn, the DO altered between low and high values, in accordance with the tidal sequence. At low tide, high values of DO were observed and viceversa. During daytime, however, this tidal effect on DO could not observed, even at 1300hrs. which showed a high value, contrary to the low value expected at high tide. This

may be due to the fact that this was the peak of sunlight intensity which drives the engines of photosynthesis. Also, warmer temperature at 1300hrs., helped speed up the rate of photosynthesis. Effect of wind can also cause dramatic change in DO. Oxygen concentration is much higher in air. When air and water meet, this tremendous difference in concentration causes oxygen molecules in air to dissolve into the water. More oxygen dissolves into water when wind stirs the water and enlarges the surface area for more diffusion to occur.

During daytime, there is a distinct variation between Stations 1 and 2, with very high values being observed at Station 2, which, therefore appears to be the most productive. At night also, a variation was observed, though of much lesser magnitude. The human settlement at Station 1, introduces more sewage into the mangrove system leading to depletion of the DO. At Station 2, DO values decreased from 1100hrs. to 1600hrs. This was in accordance with changes in temperature. Temperature is another physical process that affects DO concentration. Cold water can hold more and more of oxygen, than warmer water. Warmer water becomes saturated more easily with oxygen. As water becomes warmer it can hold less and less of DO.

Diurnally DO showed a positive correlation with temperature at Station 1. DO was highly correlated to temperature, pH and chlorophyll at Station 2 (Table C.3a-c). The high positive correlation of DO with chlorophyll suggests high primary productivity at this site.

3.5 Alkalinity

Total Alkalinity is a measure of the "buffering capacity" of water, or its ability to resist a change in pH. Aquatic systems with high alkalinity have high pH values while lakes with low alkalinity have low pH values. Alkalinity influences pH which in turn will decide the aquatic life that can survive in a water body. Alkalinity is a measure of the capacity of water to neutralize acids. Higher alkalinity levels in surface waters will buffer acid rain and other acid wastes, and prevent pH changes that are harmful to aquatic life. Because the alkalinity of many surface waters is primarily a function of bicarbonates (HCO_3^-) and carbonates (CO_3^-), and, in rare instances, of hydroxide (OH^-) ions, it is usually taken as an

indication of the sums of concentration of these constituents. These ions, called buffers, are important because they slow down the rate at which the pH changes. These are bound to cations such as sodium and potassium. Bicarbonates represent the major form of alkalinity. Without a buffering system, free carbon dioxide will form large amounts of carbonic acid that may potentially decrease the night-time pH level to 4.5. During peak periods of photosynthesis, most of the free carbon dioxide will be consumed by the plants and, as a result will drive the pH levels above 10. Total alkalinity of seawater averages 116 mg/l and is greater than that of fresh water, which can have a total alkalinity of 30 to 90 mg/l, depending on the watershed and the chemical composition of water. The brackish waters of an estuary will have total alkalinity between these values. The major factors influencing the alkalinity values of oceans are weathering of rocks, anthropogenic interferences, increase in discharge of phosphate, borate, silicate, organic acids and precipitation and dissolution of biogenic $CaCO_3$.

In most waters, alkalinity and hardness have similar values because the carbonates and bicarbonates responsible for total alkalinity are usually in the form of calcium carbonate or magnesium carbonate. Alkalinity is often related to hardness because the main source of alkalinity is usually from $CaCO_3$. If $CaCO_3$ actually accounts for most of the alkalinity, hardness in $CaCO_3$ is equal to alkalinity. Since hard water contains metal carbonates (mostly $CaCO_3$) it is high in alkalinity. However, waters with high total alkalinity are not always hard, since the carbonates can be in the form of sodium or potassium carbonate. Conversely, unless carbonate is associated with sodium or potassium, which do not contribute to hardness, soft water usually has low alkalinity. Therefore, generally, soft water is much more susceptible to fluctuations in pH from acid rains or acid contamination. Hard water lakes are generally more productive than soft water lakes and can accept more input of salts, nutrients, and acids to their system without change than can soft water lakes.

In the present study, the highest alkalinity (4.18mmol/l) was observed in the month of September'00 at Station 2 and lowest (0.183mmol/l) at Station 3 in June'99 (Table A.5). Mean values of each station were 1.41mmol/l, 1.75mmol/l, 0.922mmol/l and 1.27mmol/l for Stations 1, 2, 3 and R respectively. Results of the ANOVA revealed significant differences between stations and seasons (Table B.1). Seasonal

data (Fig. 3.5a) showed a minimum value for alkalinity during pre-monsoon at all the four stations. During all the three seasons, Station 3 recorded the lowest values. The range was 1.06mmol/l (pre-monsoon, Station 3) to 2.03mmol/l (monsoon, Station 2). Increase in alkalinity during monsoon and postmonsoon is due to the input of the carbonate and bicarbonate concentrations in the water column.

At Station 1, alkalinity is found to be correlated with pH and DO as expected (Table C.1a-d). Increase in DO causes increase in pH as explained earlier which results in high alkalinity values. Seasonal correlation data revealed (Table C.2.a-c) that alkalinity showed high correlation with hardness and salinity during premonsoon. During monsoon a high positive correlation was shown with hardness. Alkaline water limits the solubility of the common cations in it and hence showed a positive correlation with total hardness.

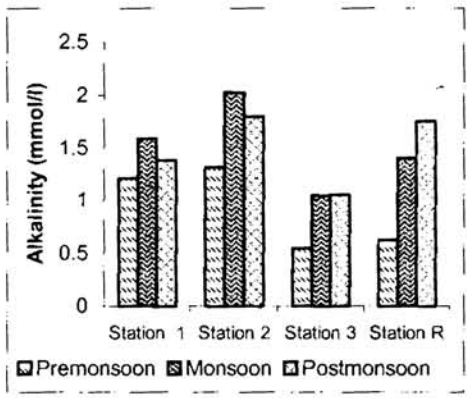

Figure 3.5a:- Spatial and seasonal variation of alkalinity

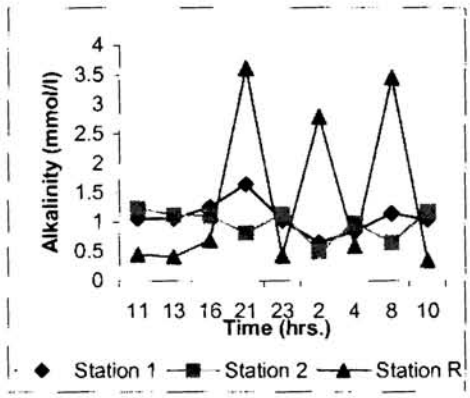

Figure 3.5b:- Spatial and diurnal variation of alkalinity

In the diurnal study, alkalinity ranged from a minimum of 0.354 mmol/l (Station R, 1000hrs.) to a maximum of 5.67mmol/l (Station R, 2100hrs.) with a mean value of 1.16 mmol/l (Fig. 3.5b). Thus, both the maximum and minimum were obtained for the reference site and hence a much variation was observed at Station R. Three higher values were observed in the diurnal study, three of them were in the reference site. For all other time, the reference site showed comparatively lower values. Station 1 and 2 showed almost similar variation, but Station R varied frequently with distinct ups and downs.

3.6 Hardness

Calcium and magnesium ions defines the extent of hardness. A low $CaCO_3$ hardness value is a reliable indication that the calcium concentration is low. However, high hardness does not necessarily reflect a high calcium concentration. In Subarnarekha river, east coast of India, total hardness ranged between 40-100 ppm during premonsoon and between 90-200 ppm during postmonsoon period (Senapati and Sahu, 1996).

In the present study, total hardness was a maximum (7.1mg/l) in April'00 at Station 1 and a minimum (0.209mg/l) at Station 3 in October'00 (Table 3.6). Mean values for the four stations were 3.41mg/l; 3.41mg/l;, 2.21mg/l and 2.72mg/l at Stations 1, 2, 3 and R respectively. For all Stations, the monsoon period showed the lowest values (Fig 3.6a). Station 2 during premonsoon showed the maximum value and Station 3 during monsoon showed the minimum. The variation between stations and seasons was confirmed by ANOVA also (Table B.1).

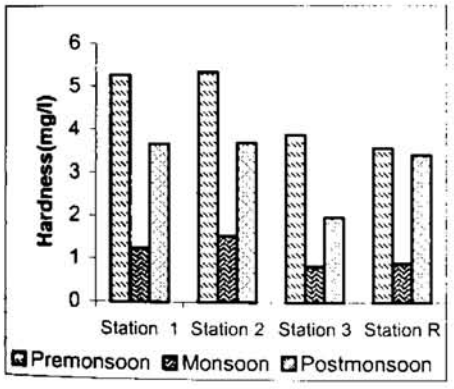

Figure 3.6a:- Spatial and seasonal variation of hardness

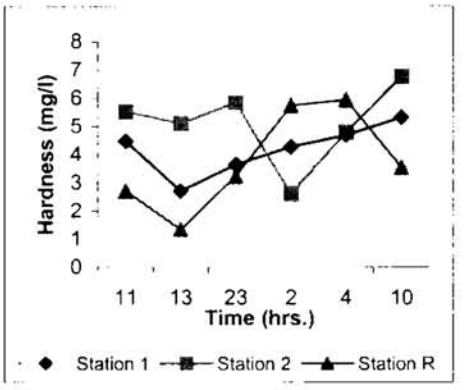

Figure 3.6b:- Spatial and diurnal variation of hardness

Total hardness in the diurnal study showed a maximum of 6.76mg/l at 1000hrs. at Station 2 and minimum, 1.36mg/l at 1300hrs. at Station R with an overall mean value of 4.36mg/l (Fig. 3.6a). Mean values for each station were 4.19mg/l, 5.12mg/l, and 3.76mg/l at Station 1, Station 2 and Station R respectively.

3.7 Total Suspended Solids (TSS)

The greater the amount of total suspended solids in water, the more turbid it would appear. The major source of total suspended solids in the mangrove waters is from mangrove litter decomposition products, phytoplankton, clays, silts from shoreline erosion, resuspended bottom sediments and allochthonous organic detritus from adjacent water bodies and/or wastewater discharges. Dredging operations, channelisation, increased flow rates, monsoonal floods, tidal activity, benthic activity etc. may also stir up bottom sediments and increase the cloudiness of the water. High concentrations of particulate matter can modify light penetration, cause shallow bays to fill in faster and smother benthic habitats-impacting both organisms and eggs. As particles of silt, clay and other organic materials settle to bottom, they can suffocate newly hatched larvae and potentially interfere with their feeding activities. If light penetration is reduced significantly, macrophyte growth may be decreased. Reduced photosynthesis can also result in a lower daytime release of oxygen into the water. Particulates also provide attachment site for heavy metals such as cadmium, mercury, and lead and many toxic organic contaminants such as PCBs, PAHs and many pesticides. The amount of suspended solids in the Mahanadi estuary, east coast of India were found to be the highest (136-151mg/l) during monsoon and the lowest (54-64mg/l) during premonsoon (Das et al., 1997). The amount of suspended solid in the water mass decreased from ebb tide to flood tide at all the three seasons. The difference was significant in the postmonsoon indicating turbid water discharge during ebb tide. The highest value was observed during low tide of monsoon indicating the maximum flow of turbid water from the upstream of the river (Das et al., 1997). The suspended particulate matter in Talapady lagoon, (India) near mangrove area showed mean values in the range 3.8 – 744.3mg/l (Nayar et al., 2000).

Monthly data of the present study showed a variation from 88.41mg/l (Station R, May'00) to 6379mg/l (Station 2, August'99) (Table 3.7). The high value at Station 2 in August'99 was due to low water content at that time due to barriers built to prevent the loss of prawn seeds.

Very high seasonal mean value was observed at Station 2 during monsoon while the lowest was observed at Station R during postmonsoon (Fig. 3.7a). TSS

showed the widest temporal fluctuation with a major peak during the monsoon months, when huge quantities of suspended particles were brought in by land runoff and also by resuspension of sedimentary particles, facilitated by the winnowing activity of the monsoon floods.

TSS showed a positive correlation with POC at all the Stations except at Station 3 (Table C.1a-d). This may be due to high tidal activity at Station 3 which flushes out TSS as readily as it forms and/or resuspension of sediment particles from the bottom. At Station 1, Station 2 and Station R, TSS was enriched with organic carbon as shown by the positive relationship between the two.

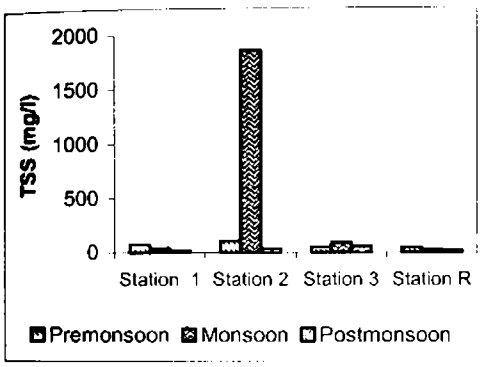

Figure 3.7a:- Spatial and seasonal variation of total suspended solids

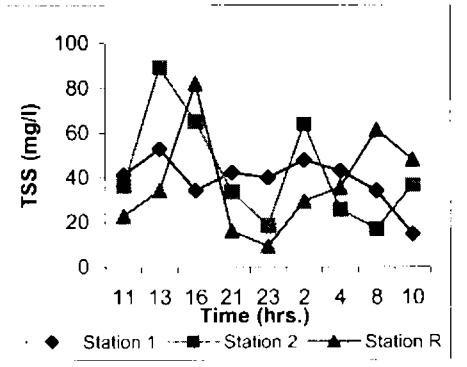

Figure 3.7b:- Spatial and diurnal variation of total suspended solids

TSS in the diurnal study varied from 9.4mg/l (Station R, 2300hrs.) to 89.33mg/l (Station 2, 1300hrs.) showing a mean value of 39.93mg/l (Fig. 3.7b). Diurnal correlation data (Table C.3a-c) showed that at Station 2 and Station R, TSS was highly enriched with POC. Absence of correlation of TSS with POC at Station 1 may be because the former was composed of large fraction some other particles like resuspended sedimentary particles, clay minerals etc.

3.8 Chlorophyll

Chlorophyll is the green pigment in aquatic plants (algae / phytoplankton) that allows them to create energy from light – to photosynthesize. Chlorophyll is a measure of all green pigments whether they are active (alive) or inactive (dead). Chlorophyll 'a' is a measure of the portion of the pigment that is still active; that is,

the portion that is still actively respiring and photosynthesising. Sunlight, temperature, nutrients and wind all affect algae numbers and therefore chlorophyll a concentration. During the premonsoon season when water begins to warm, the days are sunnier, and nutrients are plentiful, the "bloom" of algae may occur. During monsoon, and postmonsoon, when temperature and sunlight decrease, algae concentrations will decrease as well. Similarly, during day time chlorophyll 'a' concentration would increase as phytoplankton growth increases and a decrease in concentration would occur at night.

A notable feature of this component is that at Station 1, chlorophyll values were very much higher than that at the other two Stations and oscillated between 3.99µg/l (1000hrs.) and 11.09µg/l (2100hrs.) with a mean value of 6.79µg/l (Fig 3.8).

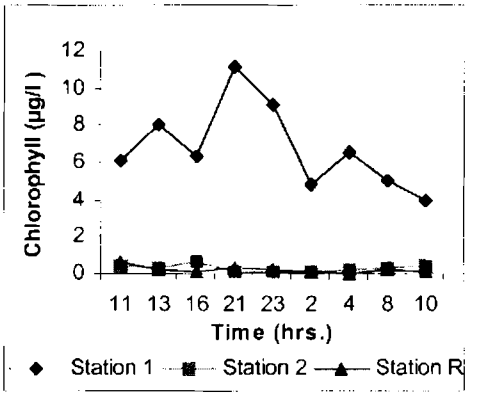

Figure 3.8:- Spatial and diurnal variation of chlorophyll

The very high chlorophyll concentration at Station 1 indicate high primary productivity at this Station. Compared to Station 1, the values were negligible at Station 2 and Station R and ranged between a minimum of 0.087µg/l (200hrs.) and a maximum of 0.687µg/l (1600hrs.) with a mean value of 0.297µg/l at Station 2 and between 0.044µg/l (400hrs.) and 0.693µg/l (1100hrs) at Station R (average 0.221µg/l). The lowest of all chlorophyll concentration was observed at Station R at 400hrs. The overall mean value was 2.44µg/l. ANOVA showed significant difference between Stations, but not with time (Table B.2).

Correlation coefficients (Table C.3a-c) showed that Chlorophyll was very much related to POC at Station 1 and Station 2 suggesting that the organic matter at

these Stations was formed mainly from the primary productivity. At Station 2, chlorophyll showed direct relationship with temperature, which may be due to the dependence of primary productivity on light intensity, as light intensity increases during day time with increase of temperature. At Station R, chlorophyll is related only to temperature and not to POC which may be due to the fact that organic matter at this Station come from other sources like sewage, anthropogenic inputs etc.

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Chapter 4

DISSOLVED ORGANIC MATTER

4.1 Introduction

Organic matter, which is present in every drop of natural water, in every particle of suspended material, can be conveniently classified into two categories; dissolved and particulate. The latter embrace material having a diameter greater than 0.45μm whereas, the former includes true dissolved matter together with colloidal materials that passed through 0.45μm membrane filter. The quantity of dissolved organic matter (DOM) greatly exceeds that of suspended or particulate organic matter (Romankevich, 1984). Dissolved organic matter, the supply and loss of which are generally balanced, is converted into a suspended state when utilized by organisms as structural material.

Dissolved organic carbon (DOC) in marine and freshwater ecosystems is one of Earth's largest actively cycled reservoirs of organic matter (Bushaw et al., 1996). The ecological significance of DOC in aquatic ecosystems include the following. DOC affects acid-base chemistry and controls the pH of many wetland waters (McKnight et al.1985). Because natural DOM is acidic and is a powerful agent for complexation of metals, it plays an important role in mineral weathering, metal toxicity and metal export (Mierle and Ingram, 1991), influencing the cycling of metals such as copper, mercury, and aluminum which, in turn can affect the concentration of trace metals found in aquatic organisms. It is a major mode of export for N and P (Qualls et al., 2002; Hedin et al., 1995) in many ecosystems and influences the availability of some forms of phosphorus and nitrogen (Bushaw et al. 1996). It is a potential source of carbon for microbial growth (Travnik, 1992) and a source of energy and nutrients to the microbial food chain. By attenuating UV radiation, it protects aquatic organisms from the harmful effects of this radiation. It also restricts the depth of the euphotic zone, stabilizes the depth of the thermocline, and depresses primary productivity in lakes (Quinby, 2000). The oxidation of organic matter affects the redox potential which, in turn, can have dramatic effects on biological and chemical processes (Breck, 1974). Under special conditions of limited circulation, complete utilization of oxygen can result in permanent or temporary reducing environments such as the Cariaco Trench, Santa Barbara basin and Black Sea. Thus, dissolved organic substances play a vital role in biological (productivity), chemical (metal complexation, flocculation and

absorption phenomena) and geological (sedimentation and early diagenesis) processes (Hayase and Shinozuka, 1995).

DOM modifies the air-sea and sediment-water interfaces. It is responsible for the foaming of seawater (Garrett, 1972) and the damping of capillary waves causing sea slicks (Barger et al; 1974). Ion exchange (Rashid, 1969), calcite precipitation (Chave and Suess, 1970) and the surface charge on particles (Neihof and Loeb, 1974) may be influenced by the organic matter. In spite of this supreme importance of organic carbon, our understanding of the distribution and cycling of organic matter in the ocean is still in a very early stage.

Enrichment of DOC in the water column occurs through degradation/ transformation of particulate organic carbon (POC), either in the water column or in bottom sediments by leaching processes, desorption of POC due to modification of environmental conditions (salinity, pH, etc.) and diffusion from interstitial water. DOC elimination processes in estuarine environment include flocculation, adsorption and degradation (Mannino and Harvey 1999). The production of soluble organic nutrients is, of course, biological but dissolution and sorption are mainly by geochemical mechanisms. Various mechanisms of retention of soluble organic nutrients can be classified as geochemical, hydrological, and biological. The most important geochemical mechanisms leading to the retention of dissolved organic nutrients is the equilibrium adsorption to Fe and Al oxyhydroxides, clays and/or whole mineral soil samples (Qualls et al., 2002). Hydrogen bonding is important in controlling soluble organic - solid organic interactions sorption (Qualls et al., 2002). Van der Waals forces are also often implicated in organic - organic sorption behavior (Leenheer, 1991). Adsorption/desorption had the effect of buffering concentrations of DOM in both mineral and organic horizons. Microbial dissolution is undoubtedly important in decomposition of cellulose, hemicellulose, proteins, and lignin in the sense that these macromolecules must be broken down into monomers which can enter the cell.

Sunlight penetrating the water surface can promote transformations of dissolved organic matter (DOM) in the photic zone. Photochemical transformations of DOM may have an important impact. Photochemical oxidation of biologically refractory DOM may form biologically labile products, thereby providing a potentially important removal mechanism for this pool of DOM. DOM is known to

be an important light absorbing component of natural waters, and hence has an important role in aquatic photochemical processes. Photochemical transformations of DOM occur upon direct absorption of UV and visible light by organic chromopores in aquatic environments (Frimmel, 1994).

Much of the emphasis on the cycling and leaching of nutrients in mangroves has been focused on inorganic nutrients. Relatively little is known about DOC cycling in coastal wetlands, although wetlands have high DOC concentrations and could be an important source to estuaries. Although it is understood that the high concentrations of DOM originate from plants, yet to our knowledge, there has been not enough seasonal study focusing on composition of DOC constituents in a wetland or tidal stream. Organic matter in mangrove environments is composed of labile and refractory compounds whose relative importance might have profound implications for organic matter diagenesis and turnover (Rowe and Deming, 1985; Fabiano et al., 1995). Conversely, the refractory fraction of OM is largely composed of complex macromolecules (like humic and fulvic acids and complex polymers), which are degraded slowly, subjected to burial, and thus lost in the short-term for the benthic food webs (Fabiano and Danovaro, 1994). This residual fraction of the organic carbon is that part of which is not accounted for by lipids, proteins and carbohydrates and consists of complex molecules like tannin and lignin, humic substances etc. A significantly improved understanding of the biogeochemical roles of carbon is of critical importance to major societal issues such as regional and global climate, the sustainability of major ecosystems, and environmental quality.

4.2 Labile Organic Constituents

A small and perhaps variable component of the dissolved organic material consists of the compounds typically associated with the general biochemical machinery of living organisms. Included in this group are amino acids, proteins, carbohydrates, lipids etc. Carbohydrates and amino acids are biochemical components comprising substantial portions of living biomass (80% of algal carbon and 65% of terrestrial plant carbon) and are important components of DOM in freshwater, in estuaries, and in the ocean. Many of these compounds are essential in life processes and probably undergo fairly rapid biological transformations and

degradation and hence highly are highly labile (Fichez, 1991; Danovaro et al., 1993; Fabiano et al., 1995; Cividanes et al., 2002).

➢ ***Amino acids***

Amino acids in aquatic systems have been categorized in terms of dissolved free amino acids (DFAA) and dissolved combined amino acids (DCAA). DCAA represent the largest well-defined molecular forms of dissolved organic matter and the largest identified component of dissolved organic nitrogen in water (Keil and Kirchman 1993) engaged in key roles in carbon and nitrogen cycling in aquatic environments. Most amino acids in living organisms are present as constituents of proteins (Billen, 1984). Little is known about the chemical structure of DCAA, which may contain many types of bound amino acids. These types include proteins and oligopeptides (Lee and Bada, 1977), amino acids adsorbed to clays or other materials (Hedges and Hare, 1987) or amino acids in humic and fulvic substances (Poutanen and Morris, 1985). Amino acids and proteins associated with melanoidins, also contribute to the DCAA pool (Keil and Kirchman, 1991).

DFAA are important intermediates in the aquatic nitrogen cycle (Lomstin et al., 1998). They are the building blocks of proteins and thereby represent one of the most important organic nitrogen components in most aquatic organisms (Landen and Hall, 2000). Free amino acids are constantly being released into surface waters as excreta from a variety of aquatic organisms and by the hydrolysis and decomposition of biological detritus. The low DFAA concentrations detected imply that these molecules are rapidly removed, either by living organisms, which utilize the amino acids as a food source, or by reaction with some other organic material to produce more complex polymeric material, or by absorption onto particulate matter. Free amino acids can provide much carbon and nitrogen for bacterial growth, which in turn suggests that the DFAA is a large component of the labile DOM flux (Hoch and Kirchman 1995; Rich et al., 1996).

The dissolved combined amino acids might serve, as a food source for aquatic organisms in a manner similar to free amino acids, although the direct utilization of combined amino acids by the biota has not been demonstrated. Since the amino acids present are produced by living organisms, they should originally all be of the L-configuration. However, during the time which these compounds

remain in water they may undergo partial racemization (Bada and Lee, 1977) and the extent of this racemization could be an indicator of the age of dissolved combined amino acids in aquatic systems. The DCAA have shown to support some bacterial growth (Rosenstock and Simon 1993). The DCAA pool probably plays an important role in cycling of nitrogen in a variety of aquatic systems (Coffin, 1989; Burdige and Martens, 1988).

The mean concentration of total dissolved amino acids in seawater (free and combined) is approximately 50µg/l (range of 20 to 250µg/l) (Millero and Sohn, 1992). Sigleo and Macko (1985) found that the total DFAA concentrations in the Patuxent estuary, Maryland, USA were around 0.06 to 0.2 µM. The DCAA were most abundant than the DFAA by a factor of 50 (Sigleo and Macko, 1985). Jorgensen, (1982) reported greater seasonal differences in a shallow estuary in Denmark where DFAA concentrations of 0.7 to 2.5 µM occurred in spring and fall, and lower concentrations (0.2 µM) in summer and winter.

Monthly and seasonal data of the present study for both dissolved total amino acids (DTAA) and dissolved combined amino acids (DCAA) showed similar variation, since DCAA was the major component of DTAA with only a minor fraction of free amino acids (Table A.8; A.9; and A.10). The concentration of free amino acids is normally 4 to 10 times less than that of the combined forms (Millero and Sohn, 1992). The DFAA were utilized at about the same rate as they were formed by extracellular release, or by the hydrolysis of DCAA and particulates (Sigleo and Macko,1985).

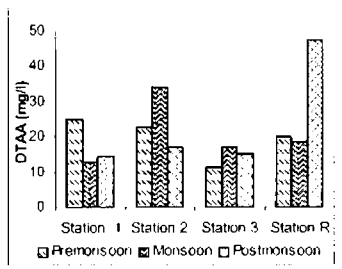

Figure 4.1: Spatial and seasonal variation of dissolved total amino acids

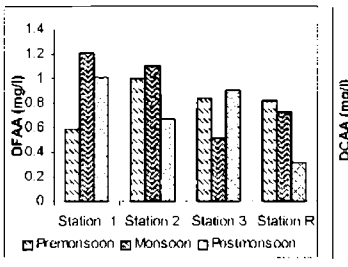

Figure 4.2: Spatial and seasonal variation of dissolved free amino acids

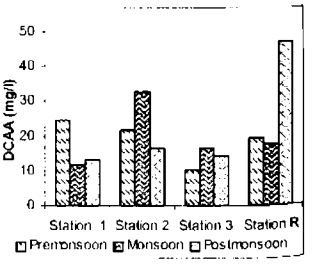

Figure 4.3: Spatial and seasonal variation of dissolved combined amino acids

Maximum values of DTAA and DCAA were at Station R, in the month of December'00 and were 73.44mg/l and 72.98mg/l respectively. In September and

December, the rainfall was very low. The low rainfall during September and December reduces the possibility of flushing and causes the amino acid components to remain in the system itself. This could explain the high values observed. For DFAA, the maximum was at Station 1, in September'00 (3.46mg/l). In September, the condition might quite favorable for the hydrolysis of combined amino acids to free forms either biologically or chemically. But in December, the environmental condition might not be favorable for intense biological or chemical activity for DCAA hydrolysis resulting in its accumulation. Lowest values were at Station 1 in July for DTAA (2.58mg/l); at Station R in October, (00) for DCAA (2.24mg/l) and at Station R in July, (00) for DFAA (0.463mg/l), which might be due to the dilution effect of rainfall.

DTAA and DCAA values at Station R showed significantly higher concentrations, the highest being observed during post monsoon (Fig 4.1 and 4.3).. This might be due to fish processing activities at this station. The lowest was observed at Station 3 during premonsoon for both these fractions. Annual mean values observed were 16.6mg/l, 23.29mg/l, 13.97mg/l and 28.25mg/l at Station 1, 2, 3 and R respectively for DCAA. Similarly for DTAA they were 17.52mg/l, 24.20mg/l, 14.71mg/l and 28.89mg/l. The lower values at Station 3 might be due to increased flushing activity at this site.

Amino acids are intermediates in degradation reactions and the fate of amino acids is not always easy to predict. When water temperature increased or input of fresh organic matter increased, followed by increased mineralisation rates, no obvious pool of amino acids was built up. Most probably there was an increased production of DFAA, but higher benthic activity will also increase the assimilation and degradation rates, and amino acids are commonly used by benthic micro-organisms as a nitrogen source. However, bacterial assimilation and degradation is not the only sink for amino acids; there are other additional sinks, of which adsorption is one of the larger, which may be an important way to preserve amino acids from further degradation (Landen and Hall, 1998). It has been observed that basic amino acids become enriched on particles by adsorption onto clay minerals through ionic interactions (Henrichs and Sugai 1993; Hedges et al. 1994). The polyelectrolytic nature of humics, major components of riverine and estuarine DOM, may also mediate adsorption of basic amino acids such as lysine as well as

arginine. Adsorption of hydrophobic dissolved organic matter to surfaces is high than that of hydrophilic dissolved organic matter (Cosovic and Vojvodic, 1989 Hydrophobicity of DCAA may also be important for understanding DCA turnover. With rumen bacteria, degradation of peptides has been positivel correlated with the surface hydrophobicity of the peptide (Chen et al., 1987). I aquatic systems, hydrophobicity may partially determine the role of proteins i biogeochemical reactions (Keil and Kirchman, 1991).

A variety of marine and estuarine phytoplankton and bacteria can us dissolved organic nitrogen (DON) as source of nitrogen (Antia et al., 1991; Kei and Kirchman, 1991). Extracellular amino acid oxidation is an important pathwa of NH_4^+ regeneration and uptake in oligotrophic and low nutrient systems enriche in the labile DON (Mulholland et al., 1998). Amino acid oxidase activity i widespread across a variety of coastal and oceanic ecosystems. Under low inorganic nutrient conditions amino acid oxidation appears to represent a potentially significant, and usually ignored source of nitrogen for phytoplankton and cyanobacteria. This adds further support to the growing recognition that labile DON is cycled rapidly (Antia et al., 1991, Bronk et al., 1994). DFAA readily adsorb onto complex dissolved organic matter and particularly to polysaccharides thereby making them readily available for bacterioplankton utilization while reducing the availability of the adsorbed compared to non-adsorbed DFAA by several orders of magnitude (Schuster et al., 1998).

For free amino acid (Fig 4.2), Station 1 showed the highest value during monsoon and the lowest at Station R during postmonsoon. Annual mean values were 0.924mg/l, 0.906mg/l, 0.747mg/l, and 0.632mg/l at Station 1, 2, 3 and R respectively with an overall mean value of 0.826mg/l.. ANOVA showed that there is no significant difference between Stations (Table B.3). Low background concentrations of monosaccharides and DFAA are typically observed in natural waters because these compounds are utilized too rapidly to accumulate (Skoog et al. 1999). Even though Station R showed high values for DTAA and DCAA, DFAA values were the lowest at the same Station. This may be due to the fact that at Station R free amino acids were rapidly removed as soon as they were formed. The limited variation in concentration of DFAA is most likely due to microbial utilization. In other words, DFAA are maintained at a low constant level because they are utilized by microbes very

fficiently (Millero and Sohn, 1992). Another possible sink for amino acids is dsorption. Adsorption to organic material has been shown to be important for amino cids compared to adsorption to clay minerals (Rosenfeld, 1979a,b). Keil and Kirchman (1993) proposed that the decreases they observed in dissolved free amino cids at the Delaware bay turbidity maximum resulted from the adsorption of free amino acids onto <0.2 um clay minerals, DOM or both. It is apparent that sorption/desorption processes occur at sufficiently short time scales to affect the molecular weight distribution of DOC within turbid regions. Therefore it is likely that there is a relationship between adsorption and input of organic material, which vary seasonally as a function of variations of primary production. When amino acids have become adsorbed to a sediment particle they can survive degradation and be preserved for long time in the sediment (Gorden and Millero, 1985). One explanation for the lower DFAA concentrations may be that adsorption of amino acids was higher in the sediment. A conclusion made by Henrichs et al. (1984), from their study of Peruvian sediments, was that the major features of DFAA concentrations and compositions were probably due to production and consumption by bacteria. The seasonal signal of DFAA was suppressed probably due to removal processes (e.g., adsorption, degradation, assimilation) occurring simultaneously with DFAA production, induced by organic matter input and increase of temperature (Landen and Hall, 1998).

Correlation data (Table C.4a-d) showed that at Station 1, DTAA was found to be negatively correlated to DO and polysaccharide. The inverse relationship of polysaccharide with amino acids suggest preferential utilization of one by microbes than the other. The inverse relationship with DO at this station might be due to high zooplankton or faunal activity, respiration of which depletes most of the DO and release aminoacids as their excreta. Another possible reason is the introduction of large amount of organic matters either mangrove detritus itself or through the sewage decomposition of which also depletes DO. The positive relationship with proteins suggests that DTAA comprise mostly of proteins. At Station 2, the high correlation value of DTAA with DCAA showed that the former is composed mostly of combined forms. DTAA showed strong positive relationship with TSS at Station 3, might be due to TSS at this station may be rich in total amino acids. The strong positive relationship with proteins at Station R also give evidence that total amino acids at this station also is composed mostly of proteins. During

premonsoon (Table C.5a-c), the total amino acid content was dependent c temperature as observed from their inverse relationship. An increase in temperatu during premonsoon enhances biological activity decreasing the total amino aci content. A positive relationship was obtained with combined amino acid. Durin monsoon, DTAA showed a positive correlation with TSS. During postmonsoo the correlation data showed a pH dependence of total amino acids.

DCAA at Station 1 showed inverse relationship with DO. Alkalinity, an directly related to proteins and total amino acids (Table C.4a-d). At Station 2 th combined amino acids showed relationships only with total and free amino acid and at Station 3 with TSS and total amino acids. Similarly at Station R, onl proteins and total amino acids showed the positive relationship with DCAA. Th inverse relation of DCAA with temperature during premonsoon (Table C.5a-c) is i accordance with the fact that the degradation of amino acids by hydrolysis (eithe biologically or chemically) increases with temperature. The positive relationshi with lipids suggests that they may be from same source with same rate of leachin and degradation. The positive relationship of DCAA with TSS may be due to th fact that latter may be rich in combined amino acids. A significantly high positiv correlation was observed with pH during postmonsoon. Proteins showed a positiv relation with combined amino acids, suggesting that combined amino acids wer mainly in the form of proteins.

The direct relationship of DFAA with pH at Station 2 (Table C.4a-d), ma be due to the fact that formation of free amino acids by the hydrolysis of combine amino acids is pH dependent. The direct relationship of DFAA wit monosaccharides may be due to the same rate of formation and decomposition o these two in the aquatic system. The tannin and lignin also showed a positiv relationship with free amino acids at Station 2, which may be due to the fact tha leaching of tannin and lignin also take place at the same rate as that of free amino acids. Free amino acids showed positive relationship with total amino acids a Station 2, which might be due to the enrichment of total amino acid pool with free amino acids. At Station 3, DFAA showed relationship with POC, which explains that the POC was rich in amino acids. Seasonal correlation data (Table C.5a-c) showed that during monsoon there existed a direct relationship with salinity and inverse relationship with DO. The inverse relationship with DO suggests increased

degradation of free amino acids in aerobic conditions. During postmonsoon, free amino acids showed negative relation with proteins suggesting the hydrolysis of proteins to free amino acids. Direct relationship with POC and monosaccharides may be due to the fact that organic matter may be enriched with free acids and formation and degradation of free amino acids and monosaccharides takes place at the same rate.

➢ *Proteins*

Proteins account for more than about 50% of the organic matter (Romankevich, 1984) and 85% of the organic nitrogen (Billen, 1984) of aquatic organisms.

The results of the present study are furnished in the (Table A.11). Maximum (28.03mg/l) was observed at Station 1 in May '00 and minimum (0.079mg/l) in July and October '99 at Station 3. Mean values of each station were 11.39mg/l, 11.76mg/l, 7.6mg/l and 11.26mg/l for Station 1, 2, 3 and R respectively.

ANOVA showed significant difference between seasons, but not between stations (Table B.3). At all the four stations monsoon concentrations were the least (Fig. 4.4a). According to Chergui and Pattee (1990), the leaves entering the water in summer and autumn were most readily colonized by microorganisms. Temperature influenced overall processing most clearly by its impact on leaching. This leaching might have increased the protein concentration in non-monsoon seasons. Photochemical processes may also be important in the cycling of some biochemical compounds (Keiber and Mopper, 1987). Station 3 showed lowest concentration at all the three seasons. Except at Station R, all the three stations showed maximum during premonsoon. The high value at Station 2 might be due to its isolated environment with creeks and channels were blocked by roots, pneumatophores and also by barriers built to prevent the loss of prawn seeds. So the tidal activity was minimum at this site with low flushing out of organic matter forcing it to remain in the system itself. There is increasing evidence that, contrary to the traditional view of proteins as very labile molecules, certain protein species of bacterial origin present in the aquatic environment, may be particularly resistant to degradation (Nagata *et al.*, 1998) suggesting that some protein components are resistant to enzymatic attack and accumulate in water.

Although high molecular organic materials were refractory to microbial attack, they tend to adhere onto the surface of detritus and consequently, particles are easily formed from high molecular weight materials. Partial hydrolysis of macromolecules such as proteins and other compounds may take place on the detrital surfaces under the influence of bacterial enzymes and consequently, a portion of the macromolecules may be transformed into low molecular weight compounds easily utilized by aquatic organisms (Ogura, 1977). Macromolecular DOM may not be directly utilized by aquatic organisms, but they may be transformed into smaller compounds on detrital surfaces by bacterial activity and take part in food chains in aquatic systems.

Previous studies have shown that absorption of polymeric DOM such as protein to surfaces can occur very rapidly and that the absorption can have substantial effects on degradation rates of organic material (van Loosedrecth et al.1990, Fletcher 1991). Keil and Kirchman (1994) suggested that DOM absorbed to colloids was less easily degraded than freely dissolved DOM. Marine colloids and sub micron particles provide large surface areas which could have substantial implications for biochemical cycling in marine environment. Effect of surface area on degradation of organic matter could be stimulative, neutral (no effect), or even inhibitory (van Loosdrecht et al., 1990, Fletcher, 1991), but the results appear to vary depending on several factors, including concentration of organic matter on the surface and the nature of the interactions between organic matter and surfaces (Van Loosdrecht et al.,1990, Griffith and Fletcher, 1991, Taylor, 1995).

Proteolytic enzymes bound to bacterial cells are suggested to be responsible for high turnover of dissolved proteins (Hollibaugh and Azam, 1983). To utilize adsorbed proteins, bacteria need to remove protein molecules from the surface. Hydrolysis of adsorbed proteins are initiated only when the affinity of bacterial proteases or 'protein-binding proteins' that bind to proteineous substrates exceeds the bond strength between proteins and surfaces (Nagata and Kirchman, 1996). Mechanisms underlying variation in degradability of dissolved proteins and other dissolved organic components in aquatic systems are not well understood. One hypothesis is that labile protein is transformed into less labile protein due to abiotic modifications including adsorption, condensation and photochemical reaction (Keil and Kirchman, 1994; Nagta and kirchman, 1996). Recent research has suggested

that association of proteins with other organic components may affect greatly degradability of proteins in water (Keil and Kirchman, 1994; Nagta and Kirchman, 1996). Because of the slow turnover and close association of proteins with other macromolecules including polysaccharides, proteins probably have more chances to be modified geochemically, which may result in the formation of refractory proteins (Keil and Kirchman, 1994). This process is significantly enhanced by radiation, especially in the ultra violet (UV) range (300 to 400 nm) (Keil and Kirchman, 1994), while originally refractive DOM becomes labile upon UV exposure (Lindell et al., 1995, 1996; Wetzel et al., 1995, Graneli et al., 1996, Kaiser and Herndl, 1997, Reitener et al., 1997). However not only the light alters the availability of the labile DOM. It has been shown that labile DOM also becomes refractory due to sorption processes in sediments (Keil et al., 1994, Hedges and Keil, 1995). Thus structures of macromolecular organic complexes and their interactions with bacterial assemblages could substantially influence storage, turnover and transport of dissolved organic matter especially proteins. Thus small polypeptides and free amino acids could condense and undergo a variety of reactions to produce large molecular weight DCAA (Hedges, 1978; Carlson et al., 1985; Yamamoto and Ishiwatari, 1989).

Correlation data (Table C.4a-d) showed that proteins at Station 1 exhibited positive relation with TSS, hardness, DTAA, DCAA) and POC and at Station 2, only hardness showed a strong relationship with proteins. At Station 3, pH, hardness and salinity determined the fate of proteins and at Station R this role was taken by temperature and salinity. Temperature is an important factor in controlling leaching of DOC. Based on seasonal patterns of concentration, Grieve (1991) proposed that production of dissolved organic matter increased exponentially with temperature. Christ and David (1996) showed that DOC leaching increased exponentially with temperature between 3°C and 28°C. These observed temperature effects could be due to the effect of temperature on microbial dissolution, solubility products, sorption equilibria, or even increases in diffusion out of particle matrices (Christ and David (1996). Protein at Station R was enriched in DTAA and DCAA as observed from their direct relationships. Seasonal correlation data (Table C.5a-c) showed a negative correlation of proteins with temperature and positive relationship with tannin and lignin in the monsoon

periods. Increase in temperature may increase the hydrolysis of proteins to amino acids and presence of tannin and lignin may exert an inhibitory effect on the degradation of proteins during premonsoon. During postmonsoon, proteins showed a negative correlation with POC and free amino acids and positive relationship to pH. Thus, during postmonsoon organic matter may be poor in proteins, by its hydrolysis to amino acids at low pH conditions. Positive relationship with DCAA during the same period may be due to the enrichment of combined amino acids with proteins. In the present study, dissolved proteins contributed 21.9% to 92.6% to DCAA pool, with a mean value of 55.7%. Mean values for each station were 64.6%, 55.8%, 59.8% and 42.8%. Thus the DCAA pool of Station 1 was the most protein enriched one.

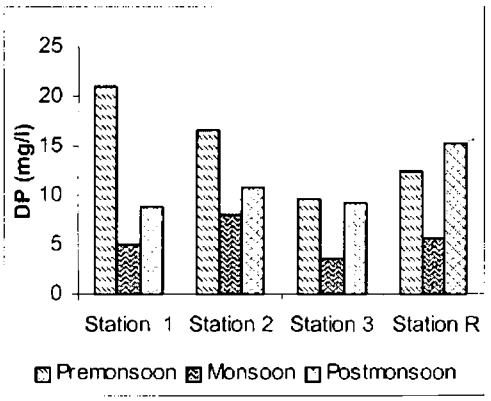

Figure 4.4a: Spatial and seasonal variation of dissolved proteins

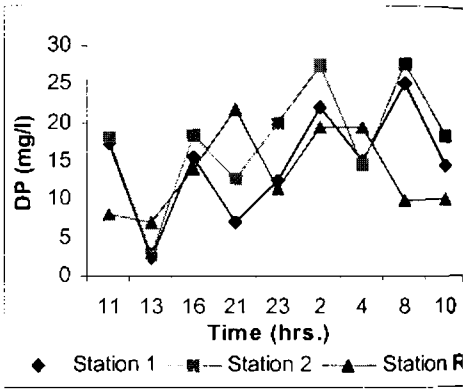

Figure 4.4b: Spatial and diurnal variation of dissolved proteins

From the diurnal data (Fig. 4.4b), protein content of Station 2 was observed to be higher than that at Station 1 showing that Station 2 was enriched with more protein. High protein content of Station R might be due to the impact of neighboring fish processing activities. Besides, all the three Stations showed the lowest values at 1300hrs.. The release of organic nitrogenous compounds has been often reported to occur during active phytoplankton growth (Bronk and Glibert, 1991; Bjørnson, 1998). However, such a low value observed at this time may be due to heterotrophic grazing and growth, and consequently bacterial DON consumption (Lara *et al.*, 1997), which may increase simultaneously with primary production. Climate warming and acidification result in faster degradation of high molecular weight substances. On the other hand, UV-B radiation has been found to break down these substances and make them available to bacterial degradation. At

hours, Station 2 had higher protein content than Station 1 (except a small crease at 4.00hrs at Station 1). ANOVA showed only a slight difference with time and no difference between stations (Table B.4).

From the correlation table for diurnal variation (Table C.6a-c) it is clear that temperature regulated the protein concentration at Station 1. Here increase in temperature may cause an increase in leaching of protein molecules from detritus. The inverse relationship of protein and chlorophyll suggests that they were of different source, the source of proteins might be other than primary production. Proteins might have produced from benthic animals, fishes, prawns etc. The correlation shown by proteins with tannin and lignin suggests they were of same source and also by the hindrance to protein decomposition in presence of phenolic compounds at Station 1. Direct relationship of proteins with humic acid suggests increased humification of the system with accumulation of these compounds onto the humics. Suppression of protein degradation in presence of humic substances may be another reason. Qualls and Richardson, (2002) observed that the humic substances appeared to inhibit biodegradation of the other fractions of the DOC since hydrophilic organic acids decomposed faster when isolated from the humic substances. At Station 2 also, proteins showed direct relationship with tannin and lignin which suggests either their common source or suppression of degradation. As at Station 1, the protein content of Station R was very much dependent on temperature and hardness. But here inverse relationship was found with temperature, which suggests that the increased temperature lead to increased microbial or chemical degradation of proteins in reference site.

- ***Carbohydrates***

Carbohydrates are the largest identified fraction of organic matter in the aquatic systems, accounting for 20-30% in surface waters (Pakulski and Benner, 1994; Benner et al., 1992; Skoog and Benner, 1997) and occur as monosaccharides, oligosaccharides and polysaccharides. They are versatile molecules that serve as energy, storage, and structural components of cells. In aquatic systems, chemical energy is stored in the form of phytoplankton-derived carbohydrates, and this in turn provides energy to non-photosynthesising organisms through the processes of glycolysis and respiration (Witter and Luther, 2002). Glucose and to a lesser extent the other dissolved neutral monosaccharide components probably fuel a large fraction of bacterial respiration (Rich et al., 1996). Previous investigation

suggested that polysaccharides are highly labile and cycled rapidly in the water column (Ittekkot et al., 1981). Carbohydrates, especially free glucose, have been shown to be biologically reactive molecules (Skoog and Benner, 1997). They have been found to vary geographically, seasonally, diurnally, and with depth and are primarily derived from phytoplankton and vascular plants.

- *Dissolved Monosaccharides (DMCHO)*

In the present study monthly data showed a highest monosaccharide concentration of 22.28mg/l at Station R in May'00 and lowest (0.783mg/l) at Station 3 in the same month (Table A.12). In the seasonal graph peak was observed at Station 2 during monsoon and minimum at Station R during monsoon (Fig.4.5a). A second largest peak was observed at Station R during premonsoon. DMCHO showed an overall mean value of 5.08mg/l. Station wise mean values were 5.02mg/l, 6.36mg/l, 4.72mg/l and 4.65mg/l for Station 1, 2, 3 and R respectively. In general, Station 2 showed the highest and Station 3 the least monosaccharide concentration. The difference was attributed to the difference in tidal activity between these two sites. The semi-enclosed area at Station 2 entails that exclusively local processes within this sector could cause the strong increases of nutrient and DOC concentrations during ebb. Creek- and rain-water are the only water sources to this mangrove swamp. The characteristic tidal signature of all parameters can therefore not be attributed to simple mixing processes of different water bodies. After inundation or rainfall, water can, however, be stored in the mangrove sediment and released again during ebb. During storage its composition is highly influenced by biogeochemical processes in the sediment. But exactly reverse is the case of Station 3., where high tidal flushing removes most of the dissolved organic nutrients from this region replacing it with fresh water.

The concentration profile of dissolved carbohydrates reflects the balance between production of dissolved carbohydrates via solubilization/hydrolysis from POC and consumption of carbohydrates by fermentative bacteria. Once hydrolyzed, most monosaccharides would likely be remineralized rapidly (Sawyer and King, 1993; Rich et al., 1996). The major monosaccharide utilizers were found to be the microheterotrophs, namely bacteria, yeasts, and possibly some algae. Their concentrations were found to be highly variable with respect to tidal cycle (Millero and Sohn, 1992). The rates at which organic carbon is actually remineralized via sulfate reduction are therefore somewhat slower than the rates at

which three specific enzymes could potentially produce monosaccharides from high-molecular weight polysaccharides. These three specific enzymes are pullulanase, laminarinase, and xylanase.

From the correlation data (Table C.4a-d) it is clear that monosaccharides at Station 1 decreases with increase of temperature, DO and alkalinity. Increase of temperature, dissolved oxygen and alkalinity might have resulted in increased microbial utilisation of monosaccharides. Polysaccharides showed a negative correlation with monosaccharides. This may be due to the hydrolysis of polysaccharides to monosaccharides. The rate-limiting step for the consumption of monosaccharides would thus be the hydrolysis of polysaccharides. At Station 2, positive correlation with TSS suggests that suspended matter may be composed mostly of particulate monosaccharides and monosaccharides may be formed by the leaching from the suspended particle. The direct relationship of tannin and lignin and free amino acids with monosaccharides suggest either their same rate of formation from the same source ie. mangroves or suppression of monosaccharide decomposition. Station R also showed a strong relationship with tannin and lignin, which suggests the export and same rate of leaching of mangrove detritus or suppression by phenolic compounds. Monosaccharides during postmonsoon (Table C.5a-c) showed significant positive correlation with POC suggesting the enrichment of organic matter with monosaccharides. Positive correlation of monosaccharides with free amino acids suggests that their source and fate are influenced by common environmental parameters. Negative relationship with pH may be due to their formation by acid hydrolysis of polysaccharides in the same season.

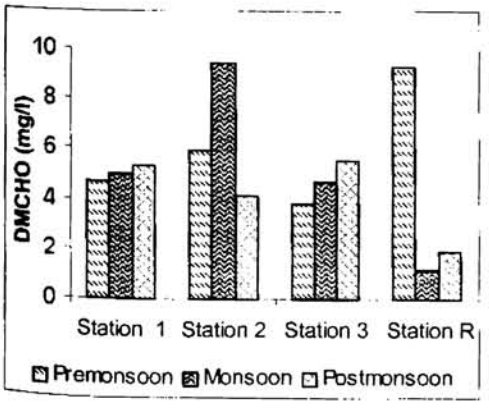

Figure 4.5a: Spatial and seasonal variation of dissolved monosaccharides

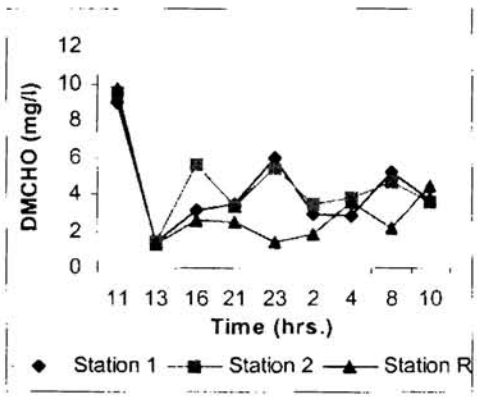

Figure 4.5b: Spatial and diurnal variation of dissolved monosaccharides

In the diurnal study, at 1100hrs., all the three Stations showed the highest monosaccharide concentration and similar to proteins, at 1300hrs. all showed the lowest values (Fig. 4.5b). Highest (9.76mg/l) and lowest (1.29mg/l) DMCHO were observed at Station R (average being 3.28mg/l). Station 1 and 2 showed almost similar variations. Omitting the values at 2300hrs. and 800hrs., variations at Station R resembled that of the other two. Thus, for the three stations maximum was observed at 1100hrs. and minimum at 1300hrs. This may be due to the increase in primary production followed by intense microbial degradation with increase in temperature and light radiation. Dissolved carbohydrates which are largely released by phytoplankton, with smaller contributions from zooplankton and bacterial excretion, as well as other minor sources, are important bacterial substrates and their levels are controlled largely by biological processes (Millero and Sohn, 1992). ANOVA showed a significant difference with time and no difference with stations (Table B.4).

Diurnal correlation data (Table C.6a-c) showed an inverse relationship for monosaccharides with total lipids suggesting preferential utilisation of the former by microbes at Station 1. At Station R, DMCHO showed a positive relationship with chlorophyll, which might be due to the fact that monosaccharides were the result of primary productivity. Direct relationship of monosaccharides with humic substances at Station R may be due to the suppression of monosaccharide degradation in presence of humic substances.

- *Dissolved Polysaccharides (DPCHO)*

The present study showed monthly variation with highest (88.04mg/l) at Station R for the month of December'00 and lowest (3.28mg/l) in August'99 at Station 2. In December, all Stations showed the highest polysaccharide concentration (Table A.13).

The seasonal graph revealed that premonsoon was associated with lowest polysaccharide concentration at all the four stations (Fig. 4.6a). The peak was shown by Station R during postmonsoon and lowest by Station 1 during

premonsoon, with a mean value of 24.69mg/l. Mean values of the four Stations were 22.26mg/l, 24.13mg/l, 25.85mg/l and 25.93mg/l.

DPCHO at Station 1 showed positive relationship with DO and negative with monosaccharides (Table C.4a-d). This suggests the formation of monosaccharides by the hydrolysis of polysaccharides. At Station 2 also polysaccharides were very much dependent on DO. The direct relationship with DO suggests the microbial degradation of mangrove detritus in aerobic condition resulting in the leaching of polysaccharides. Positive relationship with humic substances during monsoon (Table C.5a-c) may be due to the humification of system with the accumulation of polysaccharides, or may be due the inhibitory effect exerted by humic substances on the degradation of the macromolecules.

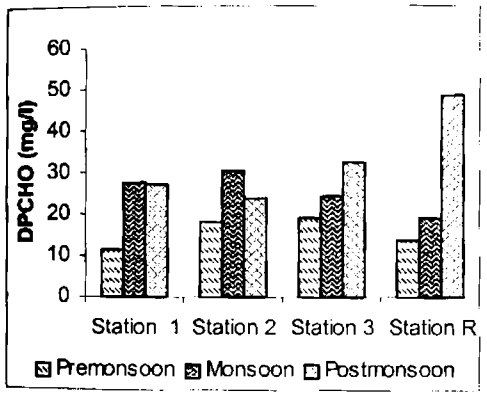

Figure 4.6a: Spatial and seasonal variation of dissolved polysaccharides

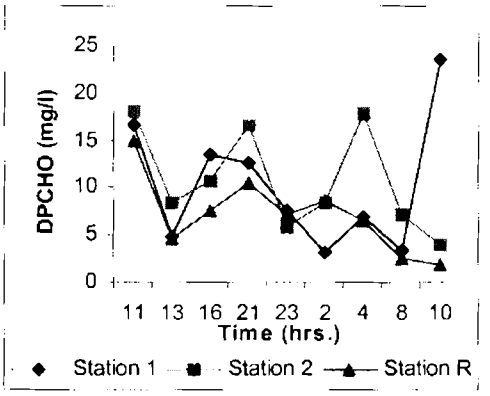

Figure 4.6b: Spatial and diurnal variation of dissolved polysaccharides

Diurnal variation showed the highest polysaccharide concentration of 23.59mg/l and lowest of 1.84mg/l at 1000hrs. at Station 1 and Station R respectively (Fig. 4.6b). Mean value observed was 9.39mg/l. From the diurnal correlation coefficients (Table C.6a-c), it is understood that polysaccharides showed positive correlation with TSS and inverse relationship with POC. This means that TSS may be enriched with particulate polysaccharides, leaching of the same would lead to the increased level of dissolved polysaccharides, DPCHO. The same process might have resulted in the simultaneous depletion of POC. Polysaccharide showed positive correlation coefficients with chlorophyll and humic acid at Station R, similar to that of monosaccharide relationships.

➢ ***Lipids***

There are significant variations in the flux and composition of lipids in the water column as a function of surface water productivity, the species composition of plankton in the surface waters, diagenesis and remineralization of organic matter as it transits the water column towards the sediments and alteration processes at the water – sediment interface. Sources and composition appear to be important factors in degradation of fatty acids. Selective degradation of particulate lipids determines the composition of dissolved high-molecular mass lipids. Differential lability of individual lipids promotes selective release of particulate lipids to the HDOM pool with subsequent selective utilization within the DOM pool (Mannino and Harvey, 1999). Nagata and Kirchman (1992) have shown that heterotrophic flagellates grazing on bacteria release lipid-rich macromolecular DOM.

Monthly data of the present study showed a peak lipid content (4.74mg/l) at Station 2 in September'00 and the minimum 0.017mg/l was observed at Station 1 in April'99 (Table A.14). Mean values at Station 1, 2, 3 and R were 0.757mg/l, 0.822mg/l, 0.388mg/l and 0.430mg/l respectively. As in the case of proteins and carbohydrates, lipids were also maximum at Station 2 and minimum at Station 3. ANOVA results confirmed the significant variation between stations, but there was no difference between seasons (Table B.3). Although lipids comprised a small fraction of dissolved organic matter, the amounts observed were significant.

Correlation data for the four stations (Table C.4a-d) showed positive relationship of lipids with dissolved oxygen, which suggests their microbial or chemical leaching from organic matter in oxic media. Total lipids during premonsoon (Table C.5a-c) showed inverse relationship with temperature and significant positive relationships with particulate organic carbon, and combined amino acids. These correlations suggest that lipid degradation might take place rapidly at moderately high temperatures at the same rate as that of combined amino acids. Also, organic matter might be enriched with lipids. During monsoon, lipids showed positive relationships with pH and tannin and lignin. This may be due to the lipid accumulation in dissolved phase at high pH and in the presence of inhibitory compounds like tannin and lignin.

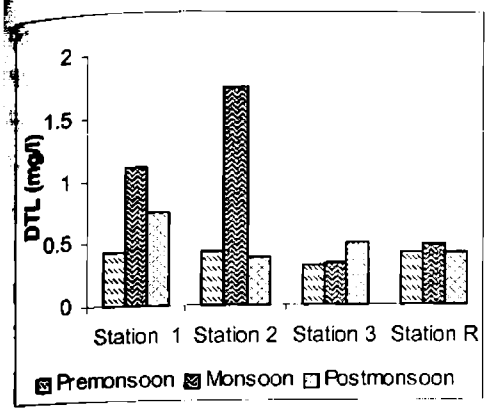

Figure 4.7a: Spatial and seasonal variation of dissolved total lipids

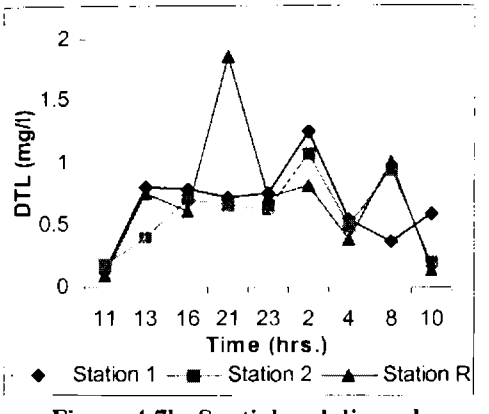

Figure 4.7b: Spatial and diurnal variation of dissolved total lipids

In the diurnal study all the three stations showed a low value at 1100hrs., with the lowest of all of 0.091mg/l at Station R (Fig. 4.7b). A high value (1.86mg/l) was observed at 2100hrs. at Station R. Station 1 and Station 2 varied almost similarly in terms of lipid content. ANOVA showed a difference in lipid content with time but no difference between stations (Table B.4). Diurnal correlation data showed (Table C.6a-c) conservative behavior of lipids with salinity at Station 1. Lipids also showed inverse relationship with monosaccharides, which suggests the preferential utilisation of the latter by microbes. At Station 2 the lipid concentration showed inverse relationship with pH, i.e., low pH leading to an increased leaching of lipids from particles and viceversa. The positive relationship shown by lipids to tannin and lignin suggests their same source. In reference site the inverse relation of lipids with DO suggests that the decomposition of lipids take place in the presence of DO and in anoxic condition, accumulation of lipids might occur. The inverse relationship of lipids in reference site with humic substances suggests lipids might take part in humification process.

4.3 Variation of Refractory Organic Constituents

➢ Tannin and Lignin (T&L)

Phenolic compounds, especially lignin, are unique constituent of vascular plants (Sarkanen and Ludwig 1971) that is typically found to be resistant to microbial degradation (Benner et al. 1986). Therefore, lignin can be useful as biomarkers for vascular plant derived organic matter in heterogenous samples such

as sediments, dissolved organic matter (Meyers-Schulte and Hedges 1986, Hamilton and Hedges 1988). The nutritional quality of the dissolved organic matter declines with increase in lignin and cellulose contents. The seasonal changes in the concentrations of natural phenolic material in aquatic ecosystems may be driven by climatic patterns that control hydrologic transport of detrital organic matter from the watershed. If climatic patterns shift significantly because of global-scale changes, the associated changes in concentrations of natural phenolic material could seriously affect the functional relationships of aquatic ecosystems.

In the present study, monthly data showed maximum T&L (2.82mg/l) at Station 1 in October'99 and minimum (0.1117mg/l) at Station R in the month of April'00 (Table A.15). Seasonal variation showed the lowest T&L concentration at Station R during postmonsoon and highest at Station 2 during monsoon (Fig 4.8a). The mean values of T&L were 1.22mg/l, 1.4mg/l, 0.533mg/l, and 0.564mg/l at Station 1, 2, 3 and R respectively. Low concentration at Station R might be due to the import of T&L from adjacent mangrove areas and subsequent removal from the water column. Several workers (Day *et al.*, 1953 ; Woodward *et al.*, 1963) have noticed that lignin – like compounds may be removed in large quantities from the water media by adsorption onto the microbial cell wall and also by processes like coagulation, sorption on particulates, dilution by receiving waters etc. The breakdown of mangrove plant tissues gives rise to a considerable variety of tannin and lignin compounds. These are readily moved about within the environment by processes like tidal effect, runoff etc. It would, therefore, seem reasonable to expect a proportion of the organic material in the estuarine waters to consist of phenolic materials like tannins and lignins. Since the mangrove environment is characterized by a number of creeks and channels through which mangrove empty their water to the neighboring estuaries, it is possible to identify mangrove-derived organic matter in the estuarine site through the identification and quantification of these compounds. Tannin and lignin of estuarine site, Station R was low compared to the first two mangrove sites, i.e., Stations 1 and 2. This may be due to the fact that tannin and lignin are of mangrove origin and a major fraction of these substances get removed from the estuarine water by precipitation or degradation as it is transported away from the mangrove environment. Dilution effect may also be one of the reason for the low estuarine concentration. Another possible reason is the adsorption by clay

minerals, organic matter etc. The concentration at Station 3 was the lowest even when compared to the estuarine site even though it is a mangrove area. The low tannin and lignin content at this Station might be due to the increased tidal activity at this site, which flushes out the organic matter as quickly as it is formed. The lignin-derived phenols in dissolved organic matter was far below the values found in sedimentary organic matter or litter. This might be due to the removal of these inhibitory compounds from the water column either by precipitation, coagulation or by adsorption onto clay minerals.

In a previous study by Kalesh et al., 2001, along the west coast of India, tannin and lignin (T&L) levels varied between 80µg/l and 147µg/l. They found a positive and negative correlation with dissolved oxygen in surface and bottom waters respectively and a negative and positive correlation with salinity at low water depths and in deep waters respectively They suggested that substances such as lignins behave more conservatively in higher salinity waters.

Correlation data (Table C.4a-d) showed that tannin and lignin was directly proportional to monosaccharides at Station 1, Station 2 and Station R which suggest the same rate of their leaching from the mangrove plant litter and proved that mangrove detritus are exported to the neighboring estuaries. It may also be due to the decreased rate of decomposition of labile compounds in presence of tannin and lignin. At Station 2, tannin and lignin was also related to TSS and free amino acids. Thus at Station 2 tannin and lignin may be formed at the same rate as that of monosaccharides and free amino acids by leaching from TSS. Here also hindrance to amino acid decomposition by tannin and lignin may be another reason. More the suspended solids more the tannin and lignin formed in the dissolved phase. During premonsoon (Table C.5a-c), tannin and lignin showed positive correlation with dissolved proteins and during monsoon with pH and total lipids. Positive correlations with proteins and lipids may be due to the accumulation of these two by low rate of degradation in presence of phenolic compounds. During postmonsoon, tannin and lignin showed an inverse relationship with temperature. This may due to the removal of tannin and lignin from the water column by increased microbial or chemical degradation at moderately high temperatures.

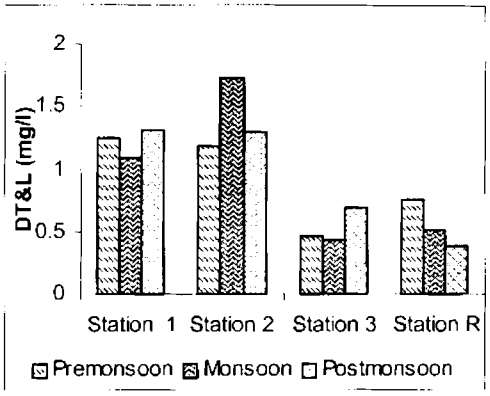

Figure 4.8a: Spatial and seasonal variation of dissolved tannin and lignin

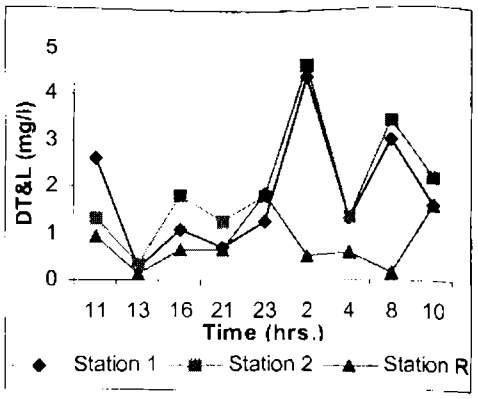

Figure 4.8b: Spatial and diurnal variation of dissolved tannin and lignin

Diurnal variation of T&L showed a ranged from 0.12mg/l (Station R, 1300hrs.) to 4.69mg/l (Station 2, 200hrs.) with a mean value of 1.55mg/l (Fig. 4.8b). Similar to proteins and DMCHO, at 13.00hrs, T&L values for the three Stations were also the lowest. Except at 200hrs., mangrove sites showed higher concentrations of T&L as expected. The higher concentration at 200hrs. in the reference site may be due to the export of mangrove detritus with the retrieving tide (since at 200hrs., low tide was observed). The two mangrove sites showed similar variation. Apart from the values at 200hrs. and 800hrs., the Station R also showed a variation similar to the mangrove site which also strengthen the hypothesis that mangroves export organic matter to the adjacent estuary. Exactly like protein, except at 1100hrs., Station 2 showed higher values than the other mangrove site, Station 1. This also confirms the fact that Station 2 produces more organic matter and is more productive than Station 1. ANOVA showed slight difference between stations and with time (Table B.4).

In the diurnal correlation data (Table C.6a-c), tannin and lignin showed a negative relationship with temperature and chlorophyll at Station 1 and direct relationship with pH. Thus tannin and lignin content at Station 1 is pH dependent. Negative relationship between tannin and lignin with chlorophyll suggests they were of different sources i.e., chlorophyll was from live plankton and tannin and lignin from mangrove detritus. Direct relationship of proteins with tannin and lignin suggests their similar source, i.e., mangroves and/or low rate of decomposition of former in presence of the latter. In reference site tannin and

lignin is negatively related only to POC, which suggests tannin and lignin may be formed by the leaching of POC in this site.

➢ **Humic Substances**

The bulk of the dissolved organic material has not been completely characterized. Large, complex humic-acid-like molecules, possibly of terrestrial origin and of considerable age, probably constitute the largest fraction. This material is probably relatively inert and therefore plays no active role in biological cycles. The source of this material and the mechanisms by which it is generated are, however, essentially unknown. Dissolved humic substances are assumed to be recalcitrant biopolymers representing at least 10% of the total marine dissolved organic carbon (DOC) pool (Ishiwatari, 1992). The occurrence of humic substance in the dissolved form is attributed to the elution of the soil organic matter (Sardessai, 1989). Shanmukhappa and Neelakantan (1989) reported a mean humic acid concentration of 10.01mg/l in mangrove habitats of Karwar, west coast of India.

In the present study, mangrove stations showed higher humic acid content than estuarine site, Station R. Monthly data (Table C.16) showed highest (28.46mg/l) in May'00 and minimum (1.62mg/l) in November'00, at Station R. Mean value of each station were 9.59mg/l, 11.13mg/l, 4.73mg/l and 2.74mg/l respectively, the overall mean value being 6.96mg/l.

All the stations showed their maximum during premonsoon (Fig. 4.9a) and might be due to increased productivity and litter fall. With low surface runoff and rainfall effect, the degraded organic matter remains within the system itself and tend to accumulate in it. Except at Station R, all the Stations showed the trend premonsoon > monsoon > postmonsoon. The trend Station 2> Station 1> Station 3> Station R was observed during all the three seasons. ANOVA also confirmed that the fluctuation between seasons and stations are significant (Table B.3). As the mangrove sites contain high organic matter, there is an increased chance of production of humic substance, which explain the high concentration of humic substance in these sites. Low values at Station R may be due to low humification and also by the subsequent removal by adsorption. The loss of dissolved humic acids in the dissolved phase could result from adsorption of humic acids onto fine

particles (Ertel et al., 1986). Low values at Station 3 may also due to the same removal process and also by the dilution effect of the active tidal waters.

Humic substances showed no significant correlations at the four stations (Table C.4a-d). But seasonal correlation data (Table C.5a-c) showed that during monsoon humic substances exhibited a positive relationship with polysaccharides, which might be due to the slow degradation of polysaccharides in presence of humic substances. During postmonsoon a negative relationships with DO and a positive relationship with tannin and lignin was observed. This might be due to the accumulation of humic substances along with tannin and lignin in low oxygen condition during this season.

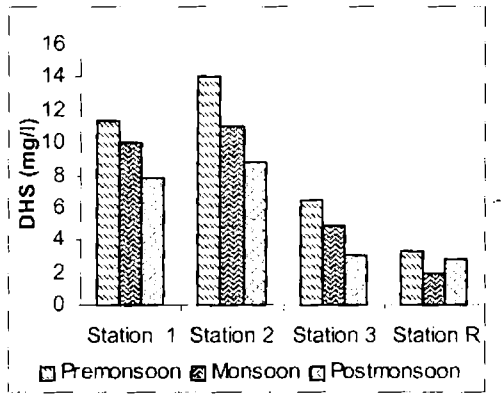

Figure 4.9a: Spatial and seasonal variation of dissolved humic substances

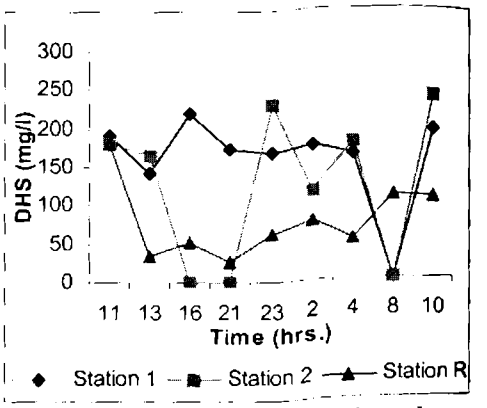

Figure 4.9b: Spatial and diurnal variation of dissolved humic substances

In the diurnal data (Fig. 4.9b) the highest value of 11.94mg/l was observed at 1000hrs. at Station 2 and the lowest value of 1.75mg/l at 13.00hrs at Station R, showing a mean value of 7.39mg/l. At Station 1, the diurnal correlation data (Table C.6a-c) showed an inverse relationship of humic substance with chlorophyll and TSS suggesting that increased primary productivity produce fresh samples of TSS with a little or no humic substance leaching out of it. Humification might occur during the period of low productivity when the TSS contains humified compounds, which leaches to the water column. Humic substance concentration was found to be directly correlated to proteins and polysaccharides at Station 1. Direct relationship of proteins and polysaccharides suggests that accumulation of proteins and polysaccharides results in humification of dissolved organic matter. It may also due to the suppression of protein and polysaccharide hydrolysis and subsequent

accumulation in presence of humic substances. The humic substances appeared to inhibit biodegradation of the other fractions of the DOC since hydrophilic organic acids decomposed faster when isolated from the humic substances (Qualls and Richardson, 2002). At Station 2, humic substances showed an inverse relationship with salinity. At Station R, humic substance was positively correlated to chlorophyll and very high with monosaccharides. This might be due to the fact that increased primary production and accumulation of monosaccharides results in humification of dissolved organic matter or it may be due to the fact that increased humic substance in the dissolved phase suppresses the decomposition of monosaccharides, which tend to accumulate in the water column. The inverse relationship of lipids with humic substance might be due to the participation and subsequent removal of lipids in humification process at this reference site.

4.3 Summary

Concentrations of dissolved organic nutrients are influenced by local plant production, decomposition, and sorption equilibrium with particulate matter and sediment. While biological factors, plant production and microbial decomposition are important in producing potentially soluble organic nutrients, physicochemical sorption equilibria, hydrology, and degradation by solar radiation are also likely to control the concentration of this material. Dissolved organic matter concentrations were generally low at Station 3 as a result of dilution with low- DOM water from nearby freshwater sources, flushing by increased tidal activity and also due to low plant density. Flushing of organic matter during rain events also influenced dissolved organic matter concentrations. Variability in rainfall accounted for the variability in DOM concentrations at Stations 1 and 2. The concentrations of Station 3 were comparable with that at the estuarine reference site, Station R except for proteins and amino acids. But at Stations 1 and 2, anthropogenic inputs, isolated condition with low to medium tidal activity and high plant density contributed to the accumulation of organic matter and its constituents. Organic matter load of these sites was higher than that of the neighboring estuary. Concentrations of proteins and amino acids at this reference site were, however, similar to that at the mangrove site, which can be attributed to the fish processing activities at that site.

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Chapter 5

PARTICULATE ORGANIC MATTER

5.1 INTRODUCTION

The particulate matter in the aquatic systems results from ongoing physical, chemical, biological and geological processes, which may vary seasonally. These processes include the supply of inorganic and organic substances from river runoff, resuspension of previously deposited sediments, production and breakdown of biological materials, and physico-chemical adsorption-desorption processes related to redox reactions near water-sediment boundry (Feeby et al., 1986). Particulate matter comprises a large fraction of the organic material in estuarine and coastal waters. The organic fraction of particulate matter includes mainly living organisms and other decay and metabolic products (Riley and Chester, 1971). In surface layers, variation in composition of organic matter may be due to variation of phytoplankton species or to variable ratios of the constituents of the particulate matter. In deep waters, detritus is the principal constituent of particles and the variations are due to the differential decomposition of the material (Montegut and Montegut, 1983). The inorganic fraction consists of quartz, feldspar, calcite, illite and chlorite formed by the weathering of terrestrial rocks. Fragments of horn blende, biotite and zircon are occasionally seen (Price and Calvert, 1973). Other inorganic species which may be seen are the silicious and calcareous remains of dead organisms and authigenic minerals, produced by the interaction of dissolved or colloidal species (Riley and Chester, 1971).

Particulate organic matter (POM) is produced by aquatic organisms through photosynthesis utilizing inorganic carbon and nutrients. Phytoplankton, benthic algae and vascular plants are the predominant groups of autotrophs, supplying most of the *insitu* primary production. Phytoplankton produces organic particles in the water column, microphytobenthos production takes place on the bottom. Macrophytes will mainly occur as detritus fragments in the water column, macroalgae may occur free-floating and still growing in the water column. Knox (1986) summarized that macrophytes (mangroves, seagrasses, *Spartina*, macroalgae) contributed 30 to 90%, microphytobenthos 5to 40% and phytoplankton 2 to 45% of the primary production.

POM in coastal water has a lead role in transportation of bioelements to the sediment and these particles are useful as foods for some aquatic organisms, thus

emphasizing their biogeochemical significance. Sinking through the water column, particulate organic matter is oxidized by microbial activity, utilizing dissolved oxygen and releasing inorganic carbon and nutrients to the water column, a process known as remineralization.

5.2 PARTICULATE ORGANIC CARBON (POC)

POM comprises both carbon and nitrogen compounds of which the carbon fraction referred to as Particulate organic carbon (POC). This may be derived from the aquatic food web or formed insitu through a complex equilibrium DOC ↔POC. The largest fraction of living material in the POC is phytoplankton and the living carbon has been estimated as 'Chlorophyll a'. POC also contains a non-living (detrital) fraction. Early studies have emphasized the importance of POC in the diet of juvenile and post larvae of shrimps, invertebrates.

In the present study, monthly POC concentrations varied as given in the Table A.17. The highest concentration (38.28mg/l) in September at Station 2 might be due to low water content and low tidal activity. The lowest (0.94mg/l) was observed at Station R in October. The annual means were 10.73mg/l, 11.39mg/l, 7.59mg/l and 6.28mg/l at Stations 1, 2, 3 and R respectively, with an overall mean of 8.68mg/l.

Seasonal variation showed a trend as depicted in the Fig. 5.1a, which showed the lowest at Station R during monsoon and the highest at Station 2 during monsoon. Of the three mangrove sites, Station 3 recorded the lowest value, which could be an outcome of intense tidal activity at this Station, which cleanses water during each flood and ebb tide. POC concentration was a maximum during non-monsoon seasons except at Station 2. This might be due to the dilution effect of monsoonal rainfall at all other Stations except Station 2. At Station 2, high POC values during monsoon might be due to heavy influx of freshwater (which introduces organic matter other than mangrove origin) or due to the resuspension of organic matter which had already settled to the bottom, by the churning action of rainfall. High organic matter recorded during non-monsoon season at all other Stations might be due to increased litter fall during this time. Dehairs et al (2000) found the Avicennia and Excoecaria litterfall to be the smallest during the period June – February. Litter fall was higher during March - June before the onset of

rainy season. Some authors reported higher litter fall in mangroves during rainy season. (Twilley et al., 1997). However, Day et al. (1987) observed that riverine mangroves in Mexico, had peak litter fall during dry season and just before the rainy season. For Kenyan mangrove ecosystem, Slim et al. (1996) also reported reduced litter fall during rainy season. The incoming water during the high tide and also the large flow of freshwater during monsoon can dilute the organic matter concentration. During premonsoon, POC showed a significant inverse relation with temperature (Table C.8a,b,c) which may be due to the higher rate of decomposition or dissolution of POC with increase in temperature. The positive correlation of POC with tannin and lignin observed during monsoon indicates that a large proportion of the POC was derived from mangrove litter. At all Stations, POC showed significant correlation coefficients with almost all-organic constituents (Table C.7a-d). At Station R, a positive relation of POC and TSS indicated enrichment of the latter with organic carbon. But TSS at all mangrove stations was poor in POC. Primary production is usually restricted because of the high turbidity, resulting in a low organic content of the suspended matter.

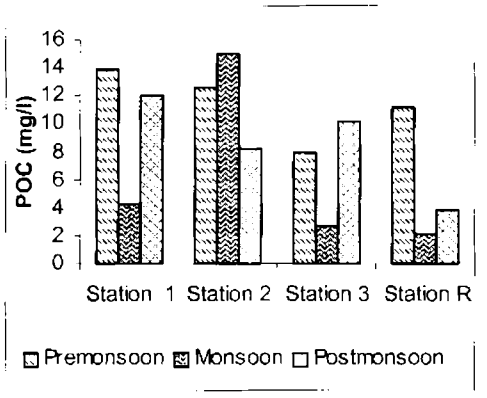

Figure 5.1a Spatial and seasonal variation of particulate organic matter

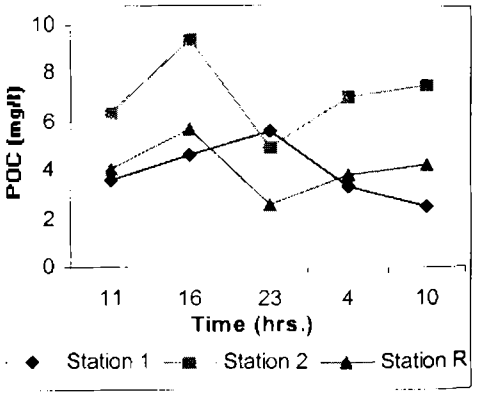

Figure 5.1b:- Spatial and diurnal variation of particulate organic matter

Diurnal variation of POC ranged from 2.56mg/l to 9.41mg/l, with a mean of 5.05mg/l (Fig. 5.1b). Except at 2300hrs., Station 2 showed higher carbon content than the other two Stations. Station R and Station 2 showed a clear-cut similar variation with smooth ups and downs. During daytime, POC at Station 1 was lower than at Station R, whereas during nighttime, the carbon content was higher at mangrove sites compared to reference site. At the estuarine site, the POC is derived

phytoplankton, algae etc., which actively contribute to the POC pool during time hours of high light intensity. But at mangrove sites, the POC mainly es from mangrove leaf litter fall which occur throughout day and night. Thus at mangrove site even though the primary production is low at night, litter composition provides a continuous flow of POC to this site. At all timings, tion 2 recorded the highest except at night when Station 1 showed the highest ue. The maximum POC at Station 2 may be due to high litter fall. It may also e to the low water content at that site which increased the density of POC in ater. Two-way ANOVA with Station and time showed significant difference ween Stations and not with time (Table B.6)

It is widespread view that mangrove forest represents an important carbon nutrient source to the adjacent lagoonal and coastal systems (Wattayakorn et al., 1990; Robertson et al., 1992). There is also evidence that this mangrove signal pidly decreases with increasing distance from the mangroves (Chandra Mohan et al., 1997; Marguillier et al., 1997; Tack, 1997). This explains the lower value observed at reference station. In mangroves, primary productivity can be attributed to several sources: the mangrove trees themselves, from their associated attached macrophytic vegetation and algae, from free-floating macrophytic vegetation, and from phytoplankton or benthic microalgae. In the estuarine system, on the other hand, primary productivity only come from the last of these sources and from terrestrial runoff and algae. The direct correlation of POC with chlorophyll at Stations 1 and 2 suggests that POC was derived mainly from primary productivity, whereas no such evidence was observed at Station R, which suggests that at Station R, POC had multiple sources including pollution by sewage, fish processing activities etc.

Similar trends were observed in other studies as well. Montegut and Montegut (1983) observed the variation of POC with depth, season and areas (Atlantic, Indian, Antartic Oceans and Mediterranean sea) and found that they were linked to fertility and changes in phytoplankton species. Shimkuz and Trimonis, (1983) observed abundance of suspended matter in the layers characterised by high productivity and density gradient in the Red Sea and Gulf of Aden. Sholokowitz and Copland, (1982) studied the chemistry of suspended matter in the Esthwaite water and found a linear relationship between phytoplankton production and

organic content and an increase in particulate matter of surface waters from 1mg/l to 7mg/l between April and late September due to productivity in that area. Pecherzewski (1980) found the POC values of the Admiralty Bay ranging from 0.22mg/l to 0.65mg/l. Danielsson et al., (1983) studied the Gota river estuary and found the particulate matter concentration to be generally close or below 10mg/l. Sajan and Damodaran, (1981) related the high organic content (12.25%) at Kallada river mouth to high rate of sedimentation in addition to primary productivity and the prevailing reducing environment. Rajendran et al., (1982) had pointed out the importance of river discharge (and monsoonal effect) on the organic carbon content of the particulate matter. Ray et al., (1984) reported that the particulate matter concentration was approximately thrice in the monsoonal months in Mahanadi river estuary, India. Nayar et al., (2000) reported POC variation in the range from 0.22 to 3.96 mg/l in Talapady lagoon, southwest coast of India. Verlencer, (1985) recorded POC in the coastal and estuarine waters of Goa to be in the range of 0.52 to 2.51 mg/l and 0.28 to 5.24 mg/l, respectively and the postmonsoonal peak was attributed to increased phytoplankton production. Sardessai (1993) recorded particulate matter in the range of 39mg/l to 310mg/l in the sediments of mangrove and estuarine ecosystems of Goa.

Organic matter in aquatic environments is composed of labile and refractory compounds (Rowe and Deming, 1985; Fabiano et al., 1995). Labile organic carbon is the fraction which is readily available to detritus feeders. A refractory pool is those with extremely long turnover times and are resistant to microbial attack. The more biochemically-labile organic compounds are preferentially consumed, leaving behind the more biochemically-stable material and a variety of alteration products (Wakeham and Ertel, 1988).

5.2.1 Variability of Labile Organic Carbon

The more labile organic matter is rapidly consumed by the intense biological activity. The labile pool, and to a lesser extent the semi-refractory pool, fuel bacterial production. The labile fraction primarily consists of simple sugars, proteins and lipids that are rapidly mineralised by bacteria and thus potentially available for higher trophic levels (Fichez, 1991; Danovaro et al., 1993).

➢ Amino acids and Proteins

Proteins and their constituent amino acids make up a substantial portion of living matter. They are typically the most abundant substances in phytoplankton and mangrove leaf litter and represent an important source of carbon and nitrogen. Protein in the phytoplankton [upto 75% of the particulate nitrogen (Nguyen and Harvey, 1994, 1997)] are rapidly recycled in the water column (Harvey et al., 1995). Combined amino acids are found in dissolved, colloidal, particulate and precipitated humic substances; in peptides, proteins, and enzymes and in living cells as well as extracellular material. Free amino acids, although present as such in extracellular and intracellular materials, are also produced by the hydrolysis of peptides and proteins in situ by bacterial and other microbial enzymatic activity. Studies on the distribution of particulate amino acids have revealed that the total particulate amino acids tend to be the maximum at the surface, where greater phytoplankton growth is observed, except at shallow water locations where suspended bottom sediment is influential (Millero and Sohn, 1992).

- *Particulate Free Amino acids (PFAA)*

Free amino acids, which are the prime metabolic products of the living organisms, exhibited a monthly variation as depicted in Table A.18. Monthly peak (1.48mg/l) was observed in May at Station 1. The values ranged between 0.034mg/l (Station R, April'00) and 1.48mg/l. Thus at all Stations except at Station 2, high values were observed in May, when evaporation could be at its peak leading to increase in the particulate free aminoacid concentration. Whereas at Station 2 dry conditions were observed in September and hence the high value of free amino acids. As in the case of POC, the amino acid showed lower values during monsoon. Station 2, however, recorded a highest during rainfall. Resuspension of organic matter or the import of extra-mangrove organic matter could be the reason. Dilution effect of the monsoonal rainfall causes a decrease in organic matter and hence in the free amino acid concentration at all other Stations. The annual means were 0.388mg/l, 0.414mg/l, 0.25mg/l and 0.217mg/l at Stations 1, 2, 3 and R respectively with an overall mean was 0.3277mg/l.

From the Fig. 5.2a, PFAA showed the highest during premonsoon at Station 1 and lowest was observed during monsoon also at Station 1. Thus, Station 1

exhibited a wide fluctuation in terms of PFAA concentration. During premonsoon, all Stations (except Station 2) recorded higher values of PFAA as a result of evaporation of dissolved phase leading to concentration of organic matter and consequently amino acids. In general, Station 2 showed the highest PFAA values, which can be explained by its isolated nature. At Station 3 values were low which are in accordance with tide.

Free amino acids showed strong interrelations with almost all organic constituents as evidenced from the correlation table C.7a-d. From the correlation data, it could be observed that, at Station 1 and Station R, TSS and POC were enriched with free amino acids. At Station 1, direct relationships of free amino acids with tannin and lignin, carbohydrates mainly monosaccharides, total lipids and humic substances suggests that their source and fate was controlled by same environmental conditions. This could also be due to the accumulation of amino acids in presence of tannin and lignin and humic substances, which slow down the degradation rate of labile organic compounds. The same is applicable to Station 1, Station 2 and Station R where a direct relation was observed between amino acids and tannin and lignin and/or humic substances. Negative correlation with combined amino acid and/or proteins at Station 1, Station 3 and Station R may be due to the formation of free amino acid by the hydrolysis of combined amino acids with simultaneous depletion of the latter. Positive correlation with temperature and DO at Station 3 may be due to the microbial degradation of organic matter to give free amino acid which is a temperature and DO dependent process i.e. microbial and chemical degradation of high molecular weight compounds to free amino acids was accelerated in aerobic condition at moderately higher temperatures. Correlation coefficients of seasonal data (Table C.8a-c) showed no significant relationship during premonsoon. During monsoon, free amino acids had direct relations with TSS, POC and all other organic moieties. Hydrographical parameters had more influence on free amino acids during postmonsoon as indicated by the linear relations with salinity and inverse relations with temperature and DO. However, only total and combined aminoacids had any decisive role in the cycling of the free form.

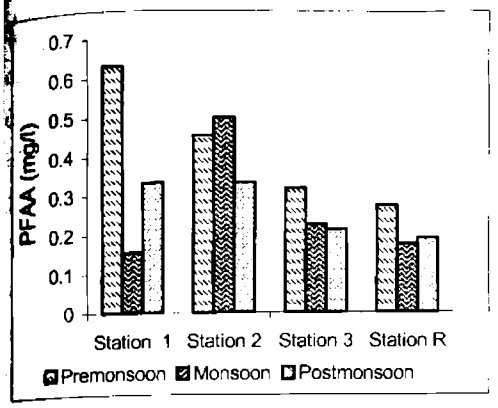

Figure 5.2a Spatial and seasonal variation of particulate free amino acids

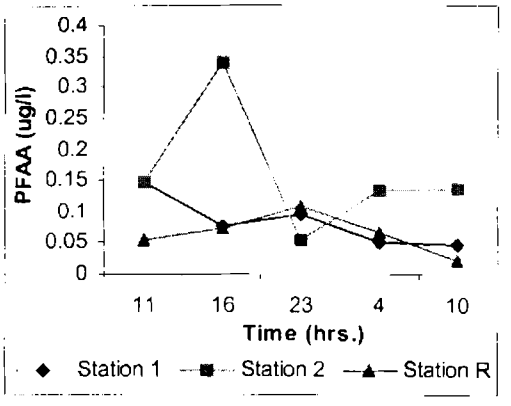

Figure 5.2b:- Spatial and diurnal variation of particulate free amino acids

Pattern of diurnal variation is depicted in the Fig. 5.2b. Station 2 showed very high mean of 0.173 mg/l. The lowest of all was shown by Station R at 1000hrs. Distribution of amino acids was in the same order as that of POC. A high value of free amino acids at Station 2 may be due to high organic matter accumulation with no way for the export. Diurnal data showed increase in free amino acid concentration during high tide and low value was observed during low tide at Station 2 and Station R. Increase in concentration during high tide may be due the import of external particles into the system. Reverse was the case for Station 1. This may be due to the dilution effect of the tidal waters. From the correlation data (Table C.9a-c) it could be concluded that the determining factors of diurnal variation of free amino acids at Station 1 were only salinity, total carbohydrates, monosaccharides and humic substances. Correlation with monosaccharides may be due to the same rate of degradation of high molecular weight compounds for these two. A positive correlation with humic substance suggests a hindrance to the degradation of amino acids, resulting in its accumulation. At Station 2, a positive correlation with chlorophyll may be due to the formation of free amino acids mainly from primary productivity and with TSS and POC highlights enrichment of suspended matter with free amino acids. Similarly at Station R the relationships were with DO, total carbohydrates, total lipids and humic substances. The negative correlation with humic substances suggests that at high levels of humic substances, microbial as well as chemical degradation of high molecular weight organic matter is inhibited, thereby lowering

the amount of free amino acids. An inverse relationship with total carbohydrates suggest a preferential utilization of sugars.

- *Particulate Combined Amino acids (PCAA)*

In aquatic environments, as elsewhere in the biosphere, combined aminoacids constitute the majority of organic nitrogen compounds. Table A.19 presents the results obtained in the present investigation. The PCAA values ranged between a minimum of 0.1mg/l to a maximum of 2.38mg/l with an annual mean being 0.612mg/l, 0.941mg/l, 0.341mg/l and 0.259mg/l at Stations 1, 2, 3 and R respectively. During all the three seasons, Station 2 showed the maximum, which may be due to low flushing activity at this site. Seasonal data (Fig. 5.3) showed the highest at Station 2 during premonsoon and the lowest at Station R during postmonsoon with a mean of 0.55mg/l. The low value at Station 3 could be attributed to high tidal influence.

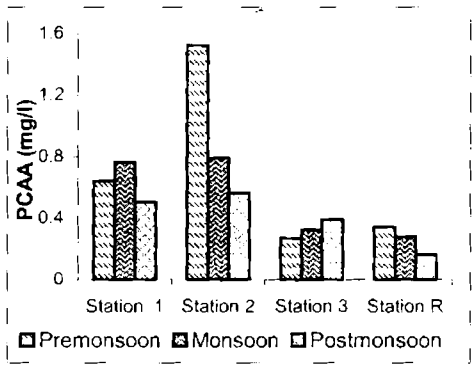

Figure 5.3:- Spatial and seasonal variation of particulate combined amino acids

PCAA at Station 1 and Station 2 exhibited significant correlation with almost all hydrographical parameters and organic entities (Table C.7a-d). At Station 1, the combined amino acids showed a significant correlation to pH. This means that the degradation of combined amino acids by the hydrolysis to form free amino acids was pH dependent. Decrease of pH to the acid side results in the increased chance of acid hydrolysis to form free amino acids and hence its removal from the system, whereas increase in pH results in its accumulation. At Station 3, PCAA showed significant correlation with proteins and free amino acids and at

Station R, only with total amino acids. Correlation with proteins suggests that the combined amino acid consist mostly of proteins. Positive correlation with total carbohydrates mainly polysaccharides suggests that their source and fate could be influenced by the same environmental processes. Positive correlation with humic substances and/or tannin and lignin was explained by the hindrance to the degradation process. Free amino acid had an inverse relation with combined form, which is due to the hydrolysis of the latter to form the free forms. A direct relationship with total amino acids suggests that the total amino acids could be composed mostly of combined fraction (PCAA). From the positive correlation of TSS and/or POC with combined amino acids it could be observed that TSS and/or POC are composed mostly of combined amino acids.

From the seasonal correlation data (Table C.8a-c), combined amino acids during premonsoon showed significant positive correlation with TSS, salinity, proteins, total lipids and total amino acids. But during monsoon, the relations were with pH and salinity and during postmonsoon, with PTAA only.

- *Particulate Total Amino acids (PTAA)*

Particulate total amino acids (PTAA) comprises small amount of free amino acids with large quantities of peptide, proteins and humic amino acid (Millero and Sohn, 1992). PTAA values peaked at Station 2 in September'00 (2.86mg/l) due to low water content during this season (Table A.20). The values ranged between 0.104mg/l (Station 3, December'00) and 2.86mg/l. PTAA showed the maximum at Station 2 during all the three seasons (Fig. 5.4). The mean values at Station 1, 2, 3 and R were 0.901mg/l, 1.36mg/l, 0.55mg/l and 0.424mg/l respectively.

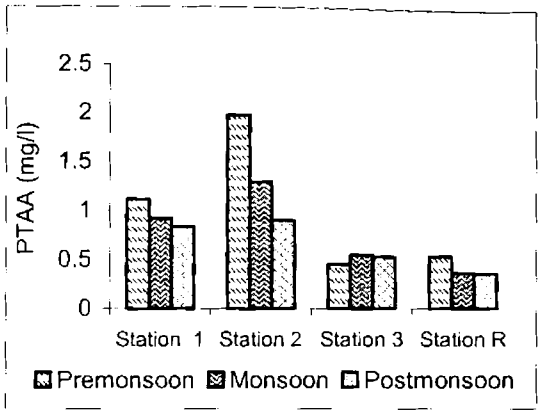

Figure 5.4:- Spatial and seasonal variation of particulate total amino acids

ANOVA showed significant difference between stations and not between seasons (Table B.5). All the Stations except Station 3 showed the same trend with the maximum during premonsoon and the minimum during postmonsoon. This may be due to evaporation of dissolved phase concentrating more and more organic matter during premonsoon or may be due to low microbial activity during this period. The low values of total amino acids observed during postmonsoon may be due to the combined effect of the southwest monsoon and high microbial activity. The maximum value observed at Station 2 could be attributed to its isolated condition without any flushing activities. Station 3, however was flushed all the time with each incoming tide, limiting the organic matter accumulation and in turn, resulting in lower PTAA levels.

Total amino acids showed the same spatial and seasonal correlations with the hydrographical as well as with other studied elements as observed in the case of combined free amino acids (Table C.7a-d and C.8a-c).

- *Particulate Proteins (PP)*

Most amino acids in living organisms are present as constituents of proteins (Billen, 1984) and proteins account for more than about 50% of the organic matter (Romankevich, 1984) and 85% of the organic nitrogen in aquatic organisms (Billen, 1984), some of which is eventually transported to the dissolved organic pool via biogeochemical processes (Tanoue, 1995).

Variation of PP in the present investigation is depicted in (Table A.21) and (Fig. 5.5a). In the monthly data, PP showed a maximum value (1.59mg/l) at Station 2 in September'00 and a minimum (0.009mg/l) at Station 3 in May'00. The means for the Stations 1, 2, 3 and R were 0.328mg/l, 0.479mg/l, 0.195mg/l and 0.149mg/l respectively. The high protein content at Station 2 might be due to high productivity (Thurman, 1986), isolated condition etc. and the low values at Station 3 could be attributed to increased tidal activity which removes POM as readily as it forms and hence proteins.

In a similar study by D'Souza and Bhosle, (2001) in the Dona Paula Bay (west of India), particulate proteins varied between 257.3 to 514.6µg/l.

The correlation data (Table C.7a-d) indicated that the protein concentration at Station 1 was dependent on all hydrographical parameters. The protein concentration was directly proportional to pH and alkalinity and inversely related to temperature and salinity. At moderately high temperature and low pH, acid mediated hydrolysis of proteins takes place more rapidly, which might be the reason for their inverse relationships. The positive correlation of particulate proteins with other studied parameters including humic substances and tannin and lignin suggested their same source and/or the accumulation of these compounds in presence of inhibitory compounds like tannin and lignin, humic acid etc. At Station 2 among the hydrographical parameters, only TSS had any significance on PP variation. This indicates that TSS was composed mostly of proteins. Correlations with other organic compounds were the same as that observed at Station 1. But at Station 3, proteins showed an inverse relationship with total lipids and positive relation with combined amino acids with no influence of hydrographical parameters. This may be due to the fact that proteins may be more rapidly degraded than lipids or vice-versa and the combined amino acids consisted mostly of proteins. Salinity is the prime parameter affecting the protein variation at Station R.

Seasonal correlation data (Table C.8a-c) showed direct relations of proteins with TSS, tannin and lignin, lipids, and combined amino acids and inverse relation with salinity during premonsoon. During monsoon, the correlations were with TSS, tannin and lignin, polysaccharides, POC and free amino acids and in post monsoon it was with polysaccharides only.

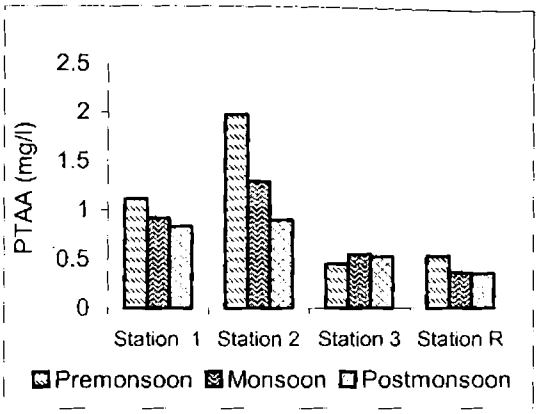

Figure 5.4:- Spatial and seasonal variation of particulate total amino acids

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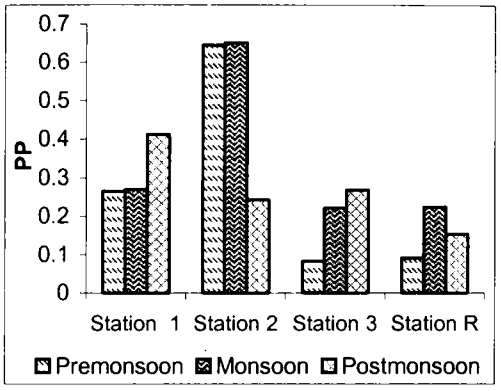

Figure 5.5a:- Spatial and seasonal variation of particulate proteins

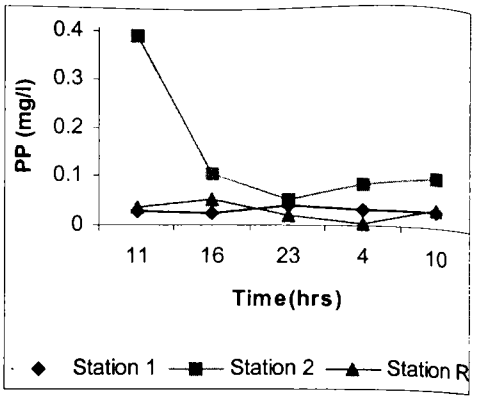

Figure 5.5b:- Spatial and diurnal variation of particulate proteins

Diurnal variation is graphically shown in the Fig. 5.5b. Station 2 showed higher values of protein concentration compared to Station 1 and R throughout the diurnal sampling as expected from the isolated location with low tidal effect or runoff. A maximum value of 0.392mg/l was observed at 11.00hrs and a minimum value of 0.004mg/l at Station R at 400hrs. No significant changes were observed in the diurnal data. Diurnal correlation coefficients (Table C.9a-c) of proteins at Station 1 showed their dependence on DO, hardness, tannin and lignin and total lipids. The inverse relationship of DO with proteins suggests the degradation of proteins via hydrolysis take place more rapidly in oxic condition. The inverse relation found between proteins and tannin and lignin and total lipids may be due to the preferential leaching of the former over the latter two. The dependence of proteins with DO, pH, salinity and humic acid at Station 2 suggests that protein degradation is dependent on the quality of the medium. The direct relationship of proteins with humic acid may be due to the suppression of the degradation of protein molecule in presence of humic acids. The inverse relationship of proteins with tannin and lignin at Station R may be due to preferential leaching of proteins over tannin and lignin. The direct relationship of proteins with POC indicates that POC was enriched with proteins and its degradation occurred at the same rate as that of the polysaccharides at this Station. There was also a strong positive correlation with polysaccharides in the same Station suggesting that the origin and fate of these two constituents are influenced by same processes.

➢ ***Carbohydrates***

Carbohydrates are major biochemicals produced by living organisms and represent a significant component of the pool of non-living dissolved and particulate organic matter in the water column (Borsheim et al., 1999; Burdige et al., 2000). The extracellular degradation of macromolecular POC to a range of organic carbon intermediates is an important part of sediment carbon remineralization (Burdige and Gardner, 1998), and carbohydrates are known to be produced and consumed as intermediates during remineralization (Arnosti and Holmer, 1999). Carbohydrate is the most important source of energy (60%) for many organisms (Romankevich, 1984; Thurman, 1985).

Carbohydrates are the structural and storage components of both marine and terrestrial organisms. In particulate samples, the contribution of carbohydrate carbon to the particulate organic carbon (POC) may vary from 10 to 30% (Hernes et al., 1996; Sigleo, 1996). They are also central to many environmental processes such as formation of humic substances (Yamaoka, 1983), removal of dissolved metals (Decho, 1990), flocculation of dissolved organic material (Mopper et al., 1995), mucilaginous macroaggregate production following eutrophication (Thornton et al., 1999) and the adhesion of microorganisms to soils and sediments (Decho, 1990). It appears that some of the carbohydrates, such as storage polysaccharides (labile sugars), are rapidly utilized by the in situ organisms during its transport from the euphotic layer to greater depths (Bhosle and Wagh, 1989; Bhosle et al., 1989). Such selective utilization of storage polysaccharides results in the accumulation of relatively less degradable structural polysaccharides (refractory sugars) as the major component of carbohydrates in particulate organic matter (Burdige et al., 2000) and therefore, are more likely to leave an imprint on the geological record. Thus, carbohydrates are useful tools in elucidating sources and metabolic path ways of organic material in aquatic environments. Phytoplankton and the detritus largely determine the carbohydrate composition of particulate matter. For example, glucose is typically present at higher levels in vascular plants. Plankton, on the other hand, are relatively enriched in ribose as compared to vascular plants (Millero and Sohn, 1992). The ratio of glucose/ribose may be used to distinguish inputs from marine and terrestrial sources, with a high ratio (>20) indicating a terrestrial source (Liebezeit, 1986). As compared with other

regions, very little information is available on the distribution of sugars in the mangroves of Cochin.

- *Particulate Total carbohydrates (PTCHO)*

Monthly variations of PTCHO are given in the Table A.22. The highest PTCHO concentration (5.12mg/l) was observed at Station 2 in September'00 and the lowest (0.028mg/l) at Station 3 in August'00. Annual mean values at Stations 1, 2, 3 and R were 1.087mg/l, 1.52mg/l, 0.812mg/l and 0.662mg/l respectively. High values of carbohydrates in mangrove stations 1 and 2 could be attributed to autochthonous input of organic matter, mainly from in situ primary production (Thurman, 1986).

The present study reflected a seasonal trend depicted in the Fig. 5.6a. Except at Station 2, all others showed a trend: premonsoon > postmonsoon > monsoon. The low values of total carbohydrates during monsoon may be due to the dilution effect. For Station 2, it was monsoon > premonsoon > postmonsoon. This may be mainly due to the monsoon runoff, which resuspend the settled organic matter back to the water column.

Total carbohydrates at all Stations showed significant positive relationships with almost all other organic constituents (Table C.7a-d). This may be due to the fact that proteins, carbohydrates, lipids, tannin and lignin, humic acids and total, combined and free amino acids were all of same origin, and degradation take place more or less at the same rate. The presence of tannin and lignin and humic substances might have a negative influence on the degradation of total carbohydrates. Also, from the correlation data it can be concluded that TSS and POC were enriched with total carbohydrates. Among hydrographical parameters, TSS showed a positive correlation at Station 1; while at Station 2 both alkalinity and TSS were significantly correlated. Temperature, salinity and DO correlated positively at Station 3. At the reference station (Station R) alkalinity showed an inverse relationship, but TSS, pH, and hardness correlated linearly.

Seasonal correlation data (Table C.8a-c) showed interrelation with tannin and lignin and lipids during premonsoon; with TSS, proteins, monosaccharides, POC, and lipids during monsoon and with proteins, polysaccharides, and lipids during postmonsoon.

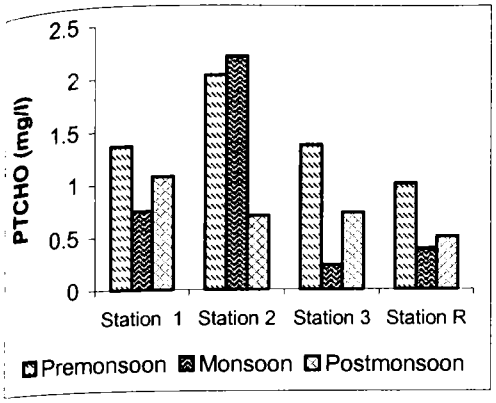

Figure 5.6a:- Spatial and seasonal variation of particulate total carbohydrates

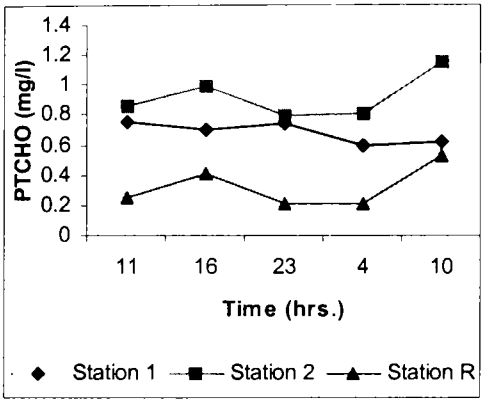

Figure 5.6b:- Spatial and diurnal variation of particulate total carbohydrates

Diurnal variations are given in the Fig. 5.6b. PTCHO values oscillated between 0.206mg/l (400hrs., Station R) and 1.15mg/l (1000hrs., Station 2) with a mean of 0.641mg/l. ANOVA showed significant variation between Stations and not with time (Table C.6). In general, total carbohydrates showed lower values at low tide and higher values at high tide. This might be because low tide creates an anoxic condition, resulting in lower primary productivity and a corresponding decrease in carbohydrates. At high tide, the reverse might have occurred. Diurnally, total carbohydrates showed significant direct correlation (Table C.9a-c) with total lipids at Station 2. This may be due to their same rate of degradation. At Station R, the direct relationship shown with humic acid may be due to an accumulation of total carbohydrates in the presence of humic acid. The inverse behavior of total carbohydrates with DO suggests a moderately high rate of degradation of carbohydrates on exposure to oxygen. Station R exhibited a strong positive correlation between total carbohydrates and polysaccharides. This may be due to total carbohydrates being composed mostly of polysaccharides.

- *Particulate Monosaccharides (PMCHO)*

The results of the present study is given in the Table A.23. In the present study, PMCHO showed a maximum (2.17mg/l) at Station 2 in May'00. The lowest, 0.020mg/l was observed at Station 3 in Aug'00 and annual means at Stations 1, 2, 3 and R were 0.572mg/l, 0.611mg/l, 0.311mg/l and 0.380mg/l respectively.

Seasonal trend (Fig. 5.7a) was the same as that for PTCHO at Station 1, Station 3 and Station R with the highest being recorded during premonsoon and the lowest during monsoon. But at Station 2, the trend was premonsoon > monsoon > postmonsoon. ANOVA (Table B.5) showed significant difference between seasons.

In a similar study by D'Souza and Bhosle, (2001) on particulate carbohydrates in the Dona Paula Bay (west of India), PMCHO varied between 101.5 to 719.4μg/l.

Results of correlation analysis (Table C.7a-d) showed that at Station 1 monosaccharide had direct relationships with every other organic constituents with the exception of proteins which can be explained as before as their same rate of formation from the same source and/or accumulation of these compounds in presence of humic substances and phenolic compounds. TSS and POC were enriched with monosaccharides as observed from their positive relationship. Stations 2 and 3 showed a similar trend. The positive correlation of monosaccharide concentration with temperature at Station 3 could be explained by the increased formation of monosaccharides by the hydrolysis of polysaccharides at moderately high temperatures. At Station R also, TSS was enriched with monosaccharides.

Seasonal correlation data (Table C.8a-c) exhibited a positive correlation of monosaccharides with salinity during premonsoon and with polysaccharides and total carbohydrates during monsoon.

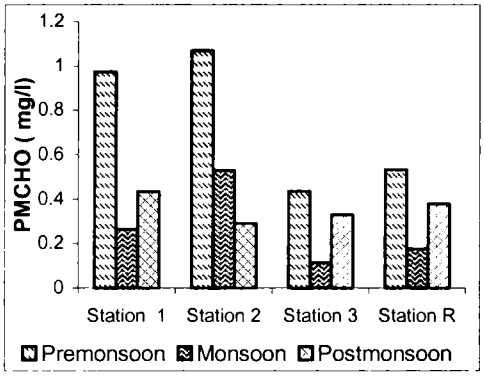

Figure 5.7a:- Spatial and seasonal variation of particulate monosaccharides

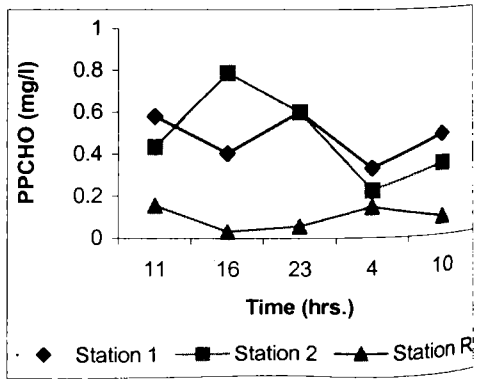

Figure 5.7b:- Spatial and diurnal variation of particulate monosaccharides

The diurnal variation was as shown in the Fig. 5.7b. PMCHO varied diurnally between 0.032mg/l (1600hrs., Station R) and 0.788mg/l (1600hrs., Station 2) with a mean of 0.351mg/l. The diurnal means were 0.474mg/l 0.486mg/l and 0.095mg/l for Station 1, 2 and R respectively. Station R showed very low monosaccharide content. Omitting the values at 1600hrs., both mangroves showed similar variation. ANOVA showed significant difference between Stations and not with time (Table C.6).

In diurnal correlation data (Table C.9a-c), PMCHO showed a positive relation with total carbohydrates at Station 1, negative relation with polysaccharides at Station 2 and with pH at Station R. This might be due to the fact that total carbohydrates were enriched with monosaccharides at Station 1 and monosaccharides were formed by the degradation/hydrolysis of polysaccharides at Station 2. The negative correlation of monosaccharides with pH at Station R was explained by the fact that shift of pH to the acid side increases the chance of hydrolysis of polysaccharides forming monosaccharides. Conversely, increasing the pH, decreases the monosaccharide concentration.

- *Particulate Polysaccharides (PPCHO)*

Spatial and monthly variations of particulate polysaccharides (PPCHO) are given in the Table A.24. PPCHO ranged from the lowest value of 0.008mg/l to the highest value of 4.19mg/l at Station 3 in Aug'00 and at Station 2 in September'00 respectively. The annual means at Stations 1, 2, 3 and R were 0.515mg/l, 0.907mg/l, 0.501mg/l and 0.282mg/l respectively. Seasonal variation (Fig. 5.8a) showed the lowest at Station 3 during monsoon and the highest was recorded at Station 2 during monsoon mean being 0.564mg/l.

In a similar study by Sigleo, (1996), particulate carbohydrate concentration was found to be in the range from 25 to 848 μg/l in the Potomac River, U.S.A.

Stationwise correlation data are given in Table C.7a-d and seasonwise in Table C.8a-c. Polysaccharides showed positive relationships with pH, and negative with temperature, salinity, and positive with all other organic constituents at Station 1. Increase of pH decreases the possibility of acid hydrolysis, resulting in the accumulation of polysaccharides. Hence a direct relationship was observed between polysaccharides and pH. An increase of pH along with decrease of

temperature and salinity elevates the amount of polysaccharides at Station 1. Direct relationship with proteins, total lipids, tannin and lignin, total amino acids (mainly combined fraction) and humic substances may be due to their same rate of degradation from the same mangrove or may be due to the suppression of the rate of degradation of polysaccharides in presence of humic substances and tannin and lignin. The direct relationship of polysaccharides with total carbohydrates suggests that the latter consists mainly of the former. At Stations 2, 3 and R also the above correlations were observed. The positive relation of TSS with polysaccharides in these Stations might be due to the enrichment of the former with the latter. During monsoon polysaccharides showed positive relations with TSS, proteins, tannin and lignin, monosaccharides, total lipids and POC, and during postmonsoon with proteins, total carbohydrates, and POC.

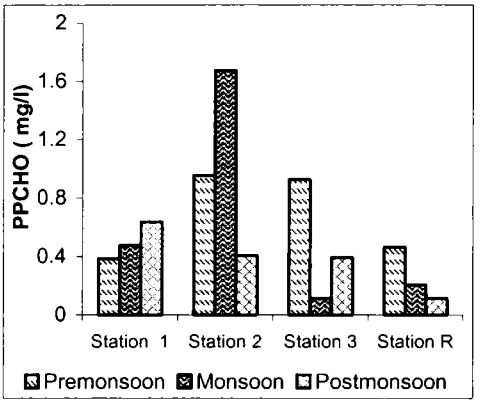

Figure 5.8a:- Spatial and seasonal variation of particulate polysaccharides

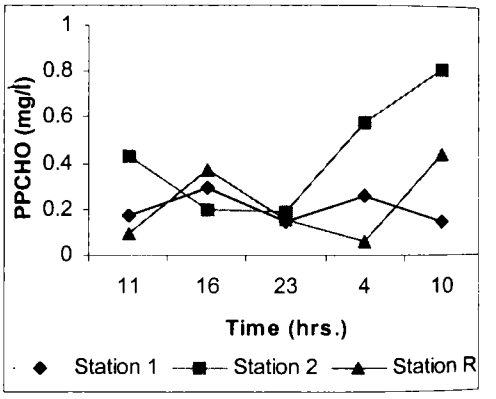

Figure 5.8b:- Spatial and diurnal variation of particulate polysaccharides

In the diurnal study (Fig. 5.8b), a maximum value (0.811mg/l) was observed at 1000hrs. at Station 2 and a minimum (0.062mg/l) at Station R, 400hrs. The overall PPCHO concentration showed a mean of 0.29mg/l. For Station 1, a mean of 0.209mg/l was observed. Station 2 and Station R showed means of 0.458mg/l and 0.233mg/l.

Diurnal correlation data (Table C.9a-c) showed an inverse relation of polysaccharides with monosaccharides at Station 1 and at Station 2, since monosaccharides are formed by the hydrolysis of polysaccharides. At Station R, polysaccharides showed relations with pH, TSS, total carbohydrates.

➢ ***Particulate Total Lipids (PTL)***

Lipids constitute a minor but important fraction of the POC due to their involvement in energy storage and use, reproduction, regulation of metabolic processes, membrane structure, etc. Although the major components of dissolved and particulate lipids were similar (n-alkanes, pristane, phytane, and fatty acid esters), particulate lipids included a substantial contribution from unresolved compounds as well as olefins, alkylated benzenes, quinones, and minor contributors not found in the dissolved fractions (Millero and Sohn, 1992).

Monthly data (Table A.25) showed a clear-cut maximum, 9.31mg/l at Station 2 in September'00 and a minimum (0.003mg/l) at Station 1 in January'00 with an overall annual mean of 0.64mg/l. The annual means for each Station were 0.44mg/l, 1.25mg/l, 0.351mg/l and 0.292mg/l. Fig. 5.9a showed spatial and seasonal variation of particulate lipids in which a very high peak at Station 2 during monsoon was observed. This might be due to influx of organic matter through surface run-off.

At all Stations, total lipids showed positive correlation coefficients with almost all entities (Table C.7a-d). The negative relationship of PTL with protein in Station 3 might be due to preferential microbial utilization of the latter. Lipids showed a general trend of positive relationship with proteins, tannin and lignin, total carbohydrates and combined amino acids during premonsoon and monsoon (Table C.8a-c). During postmonsoon the relationships were with proteins and total carbohydrates. The positive correlation coefficients of total lipids with proteins, carbohydrates, combined amino acids, tannin and lignin and humic acid may be due to their similar rate of decomposition from the same source or may be due to the suppression effect of tannin and lignin and humic substances on microbial activity. High concentrations of tannins may hamper colonization by the macrobenthos (Lee, 1999). Significantly high positive correlation of lipids with organic carbon and/or TSS may be due to enrichment of the latter with the former.

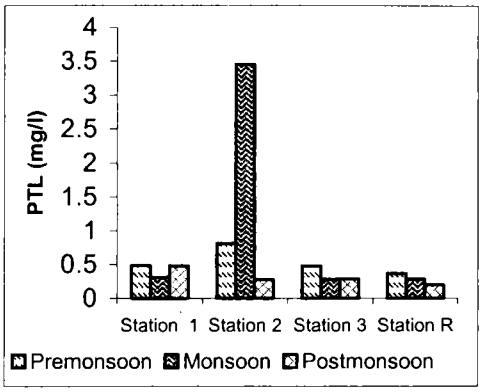

Figure 5.9a:- Spatial and seasonal variation of particulate total lipids

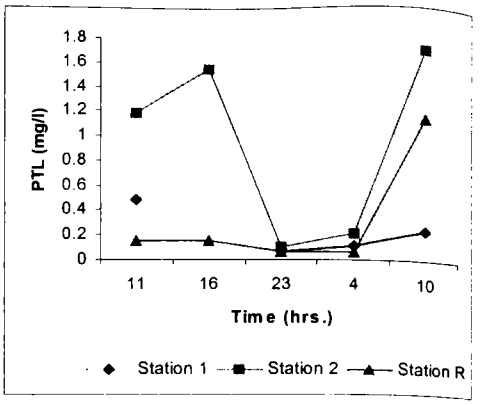

Figure 5.9b:- Spatial and diurnal variation of particulate total lipids

Diurnal data expressed graphically in Fig. 5.9b exhibited a very high PTL concentration during day time and very low concentrations at night. This is in accordance with the primary production, which is also a maximum during day and a minimum at night. Thus lipids are essentially from biological production at all the three Stations. The concentration at Station 1 was the lowest, the mean being 0.24mg/l. But Station 2 showed comparatively very high values for which mean was 0.937mg/l. ANOVA showed significant difference between Stations and not with time (Table B.6). Lipids showed correlation in the diurnal data (Table C.9a-c) similar to that observed in the monthly data. Inverse relation of DO with lipids in Station 1 might be due to increased aerobic degradation of the same. Positive correlation of lipids with chlorophyll in Station 2 suggests that the lipids may be the result of primary productivity.

5.2.2. Variability of Refractory Organic Matter

The refractory fraction of OM is largely composed of complex macromolecules (like humic and fulvic acids and complex polymers like tannin and lignin), which are degraded slowly, subjected to burial (Fabiano and Danovaro, 1994). Fichez (1991) has proposed the term 'complex organic matter'(COM) to define this residual fraction of the organic carbon, which is not accounted for by lipids, proteins and carbohydrates.

➢ ***Particulate Tannin and Lignin (PT&L)***

To date, no information is available on the contribution of lignin to the suspended particulate fraction in aquatic systems. It was in this context that field studies were undertaken to measure the concentration and variation of the lignin in suspended particulate material within 3 mangrove areas so as to learn how this material is modified during its transit through this important environmental compartment.

Monthly data (Table A.26) showed a maximum (2.75mg/l) at Station 2 in September'00 and a minimum (0.014mg/l) at Station R in October'00. The overall mean was 0.199mg/l. Annual means at Stations 1, 2, 3 and R were 0.14mg/l, 0.405mg/l, 0.124 and 0.058mg/l respectively. A maximum was observed at the mangrove Station, Station 2, and a minimum at Station R, which is a non-mangrove site. Seasonal data (Fig. 5.10a) showed a trend with all the mangrove Stations except Station 2 showing the minimum during monsoon. But for Station 2, a maximum was observed during monsoon. This could be attributed to resuspension of benthic organic matter by high runoff during monsoon. Higher particulate tannin and lignin at Station 2 might be due to its removal from the water medium by adsorption onto the microbial cell wall (Day et al., 1953; Woodward et al., 1963) and by processes like coagulation, sorption on particulates and others (Kalesh et al., 2001). It may also be due to the resuspension of the particles by the activity of benthic fauna like crabs, fishes, prawns etc. The tidal effect was, at this Station, a minimum and hence continuous flushing out of organic matter was not possible. The organic matter produced remains in the mangrove environment itself. At Station 2, the water was turbid throughout the study period. Lower values at Station 1 may be due to dilution effect by the estuarine water and also due to the sorption process after which the particles settles to the bottom due to the low density of the water, as the water was somewhat clearer than the Station 2. Low values at Station 3 might be due to the removal of tannin and lignin by each incoming tide. The lowest value observed at Station R might be due to the import of mangrove detritus to this site.

Tannin and lignin showed strong interrelationships with many other organic entities at all the four Stations (Table C.7a-d). The positive correlations shown by tannin and lignin with carbohydrates, proteins, lipids, amino acids and humic acids

may be due to the suppression of degradation of the compounds in presence of inhibitory compounds like humic substances and tannin and lignin. High concentrations of tannins might destroy microbial colonization (Lee, 1999). It may also be due to the same rate of degradation from the same source. The direct relation shown with TSS (Station 1 and Station R) and/or with POC (Station 2 and Station 3) may be due to the enrichment of these with the tannin and lignin. The positive correlation of POC with tannin and lignin indicate that a large proportion of POC was derived from mangrove litter. The tannin-POC relationship thus provides us with a reasonable index of the relative extent of mangrove input to each of these Stations (Alongi et al., 1989).

During premonsoon and monsoon also T&L showed similar relationships as observed above (Table C.8a-c). During postmonsoon tannin and lignin showed a negative relationship with pH, and a positive relationship with humic substances. Tannin and lignin consists of mostly acidic components, and hence decreasing the pH increases the concentration of these acid components and the total tannin and lignin content. Humic substances and T&L, both being refractory in nature tend to accumulate during postmonsoon.

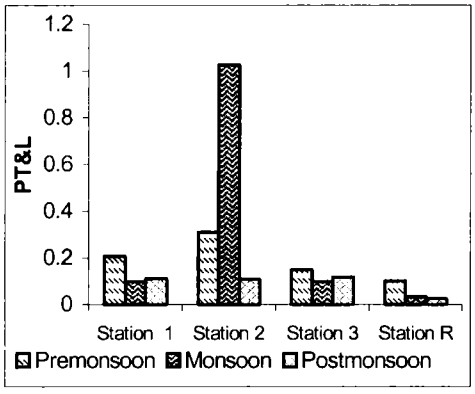

Figure 5.10a:- Spatial and seasonal variation of particulate tannin and lignin

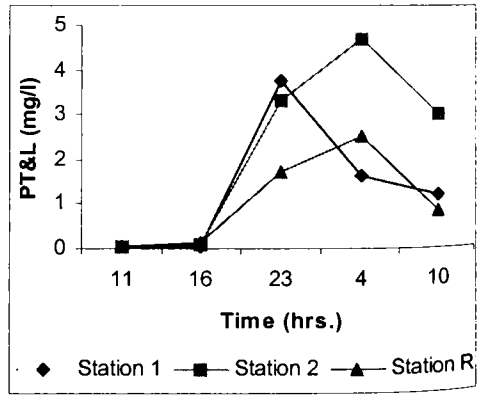

Figure 5.10b:- Spatial and diurnal variation of particulate tannin and lignin

In the diurnal variation (Fig 5.10b), PT&L were practically nil during the period 1100hrs to 1600hrs in all the Stations and high at night. This could be attributed to oxygen deficient situation at night by the decomposition of organic matter. In this oxygen deficient condition degradation of tannin and lignin may

stop abruptly resulting in the accumulation of this compound at night. Station 2 showed very high concentration (4.7mg/l) of T&L especially at 400hrs. The overall mean was 1.54mg/l with a range from the minimum value of 0.026mg/l (at Station R, in 1100hrs.) to a maximum of 4.7mg/l (at Station 2, in 400hrs.).

Correlation coefficients of diurnal variation are given in the (Table C.9a-c). Inverse relationship of tannin and lignin with DO in Station 1 and Station 2 proved that accumulation of tannin and lignin takes place in anaerobic conditions and conversely, if sufficient amount of oxygen is available, then the degradation of tannin and lignin occur rather rapidly. Inverse relationship with chlorophyll at Station 1 and at Station 2 can be attributed to the fact that they were of different sources i.e., chlorophyll may be coming from increased phytoplankton activity and tannin and lignin from the mangrove plant parts. Increased concentration of tannin and lignin in aquatic systems may reduce the phytoplankton activity in the system. Inverse relationship of temperature with tannin and lignin at all the three Stations may be due to increased decomposition of the same in moderately high temperature. Inverse relation with pH was also found at Station 2. This clearly shows the pH dependence of tannin and lignin degradation. Thus, in general, increase in temperature, DO and pH causes increased degradation of tannin and lignin in the studied systems.

- ***Particulate Humic Substances (PHS)***

Refractory particulate organic carbon (POC) is mainly constituted by carbon present in humic material. PHS is a measure of the extent of organic matter humification and aggregation in the water column before reaching the bottom and the addition of humic material through other sources like terrestrial inflow in the water column (Sardessai, 1989;1999). The PHS concentration is controlled by bacterial abundance and the labile nature of POC. Humification of organic carbon is dependent on biochemical conditions of the aquatic system. The temporal and spatial variation of particulate humic substances depend largely on the nature and extent of primary and secondary producers (Sardessai, 1989; 1999). PHS signatures in the water column are indicative of the accumulation of the fraction of non-living POC including those released by microorganisms in the form of exopolymers. Mangrove leaves, like most other nonwoody vascular plant tissues, are compositionally complex. As has been observed with other tissues (Hedges and

Weliky, 1989), the early diagenesis of mangrove leaves is a selective process, resulting in varying compositions over time. Important differences in chemical composition and diagenetic patterns appear to exist between woody and nonwoody plant tissues. Non-woody vascular plant tissues are important sources of organic matter to terrestrial and coastal marine environments and often are rich in tannins and polymethylene-type polymers that are likely precursors of geopolymers such as humic substances and kerogens (Benner et al., 1990).

Monthly variation of PHS in the present study (Table A.27) ranged from 0.208mg/l (February'00, Station R) to 7.47mg/l (September'00. Station 2) with a total mean of 1.6mg/l. Annual mean values of Station 1, Station 2, Station 3 and Station R were 1.58mg/l, 2.39mg/l, 1.69mg/l and 0.588mg/l respectively.

The observed PHS values were in the range that recorded by Shanmukhappa and Neelakantan (1989) in mangrove habitats of Karwar, west coast of India, where an average particulate humic acid concentration of 13.26mg/l was found.

Seasonal variation is depicted in Fig. 5.11a. PHS was least at Station R during all the three seasons.

Throughout the study, PHS concentration was lower than the dissolved humic substance concentration. Patches of high concentration of humic substances in the particulate matter at Station 2 was observed and could be attributed to the preservation of organic carbon due to lower microbial activity and oxygen deficient conditions. The presence of high concentration of PHS reflects the accumulation of humic material probably due to decreased bacterial activity resulting in high humification. This humification could be due to the aggregation of recycled refractory organic material. The lower concentration of humic substances at Station R may be due to negligible humification which might be a consequence of high bacterial production revealing efficient recycling of labile POC and non production of recalcitrant carbon in that area. The refractory organic material accumulates in the particulate forms and is related to spatial and temporal variations in biochemical conditions. Thus, the PHS concentration is controlled by bacterial abundance and the labile nature of POC. Mangroves are known to harbour a pool of organic matter, which is governed, by tidal action, fresh water inflow, litter fall and the rate of primary production. During monsoon, high water flow causes a

dilution effect on humic substance concentration. The export of organic matter due to tidal action from the mangrove environment is also very significant (Wattayakorn et al., 1990; Dittmar and Lara, 2001). The increase or decrease of PHS level is intricately associated with the variation in the intensity of monsoonal rainfall and the resultant flux of water and transport of particles. Furthermore, the occasional resuspension of sedimentary particles during the monsoon also plays a significant role in the increase of PHS concentration in the mangrove ecosystem. The high value of PHS at Station 2 during monsoon might be due to this effect. At all other Stations, premonsoonal maxima were observed, which might be due to high litter fall. Twilley et al. [1986] reported the highest litter fall during premonsoon and the lowest during monsoon in mangroves of southwest Florida. Lu and Lin (1990) and Tam et al. (1998) reported that eventhough litter production and fall were observed throughout the year, there was a distinct seasonal pattern with peak fall in summer seasons and very little fall in winter. High temperature, longer duration of light and higher evapotranspiration rate during summer months are probably the factors responsible for the greatest litterfall at this time (Chale, 1996) The mangrove litter undergoes degradation by bacteria and fungi. Litter decomposition rates vary significantly between plant species, affected by leaf anatomy and chemical composition (in particular, the internal nutrient and lignin concentrations). The litter fall mainly contributes to the high concentration of organic matter and humic acids observed in the premonsoon (Wafar, 1987).

A comparison of the PHS concentration at the three mangrove Stations reveals that in general, Station 2 has a high concentration of humic acids as compared to Stations 1 and 3. A thick population of mangroves characterizes station 2. Besides, the area is cut off from the estuary during the low tides, which also helps in the retention of organic matter. Station 3 receives a part of its supply of organic matter from the fresh water, which is so evident from the low salinity at this Station relative to Station 1. Station 1 is dominated by salt water for a greater part of the year and although mangrove community influences the water column, the area has free access to the estuary even during low tide.

It can be concluded that the humic acids in the particulate matter of these mangrove swamps are contributed mainly by the decomposition of the litter and partly by the fresh water influx during the monsoons. The processes like

resuspension and the variability in the transport of organic matter to the mangrove ecosystem during different seasons play a significant role in the humic acids concentration in the mangrove ecosystem. In the estuaries, the particulate humic acids form a negligible fraction of the humic acid component of organic matter and it is removed or desorbed when it mixes with saline water of low salinity range (0-5 x 10^{-3}) (Sardessai., 1993).

As observed for T&L, PHS showed significant correlations with almost all organic constituents at all the four Stations (Table C.7a-d). Also, the positive correlation of humic substances with proteins, carbohydrates, lipids, amino acids, tannin and lignin and negative correlation with DO suggests that humification occurs when the aquatic system contains heavy load of all these compounds in anoxic conditions.

Humic substances exhibited (Table C.8a-c) a positive correlation with POC, during monsoon and this could be due to the resuspension of humified sedimentary particles. The positive correlation of PHS observed with tannin and lignin during postmonsoon might be due to their refractory nature.

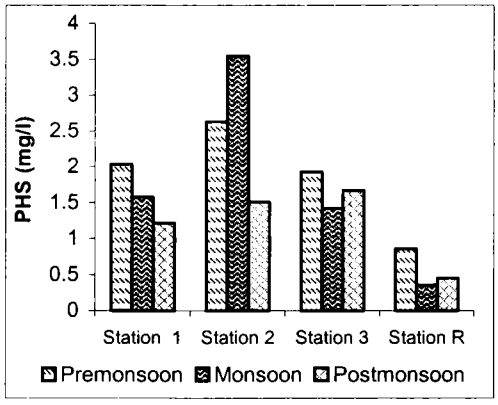

Figure 5.11a:- Spatial and seasonal variation Of particulate humic substances

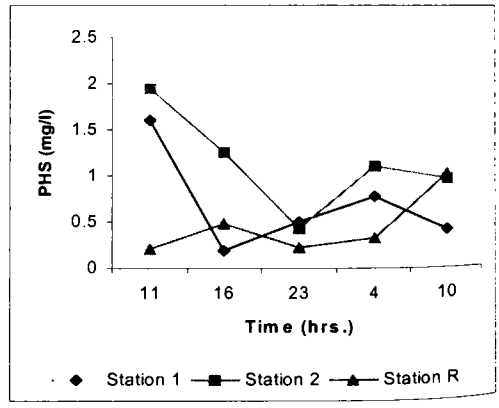

Figure 5.11b:- Spatial and diurnal variation of particulate humic substances

In the diurnal study (Fig. 5.11b), the PHS varied from a minimum value of 0.194mg/l (1600hrs., Station 1) to a maximum value of 1.95mg/l (1100hrs., Station 2) with an overall mean of 0.764mg/l. The diurnal means of Stations 1, 2 and R were 10.76mg/l, 1.16mg/l and 0.5mg/l respectively.

Diurnal data (Table C.9a-c) showed positive correlations of humic acid with pH and total lipids and inverse with salinity. At Station 2, the positive relationships were with all hydrographical parameters and with proteins. At Station R humic substances showed negative relationships with DO and positive with carbohydrates, total lipids and free amino acids. From the correlation data it could be concluded that anoxic conditions with alkaline nature and high temperature, and salinity may result in the increased humification of the particulate organic matter

5.3 Food Quality Index of Particulate Organic Matter

An evaluation of the nutritional quality was done by assuming carbohydrates, proteins and lipids as the more labile compounds of sedimentary organic matter. The sum of lipid, protein and carbohydrate carbon was expressed as biopolymeric carbon fraction (PBPC) (Mayer, 1989; Fichez, 1991; Fabiano and Danovara, 1994; Fabiano et al., 1995). PBPC is assumed as a reliable estimate of the labile fraction of the organic matter. The PBPC of POC ratio expressed as a percentage is used as a 'food index', to depict the quality of organic matter available as food to consumers (Danovara and Fabiano, 1997).

5.3.1 Nutritional Quality of Organic Matter

The relative distribution of percentages of PP-C, PTCHO-C and PTL-C to total POC appears to vary during the period of study (Tables A.28, A.29, A.30; Figs. 5.12, 5.13, 5.14 respectively). The PTCHO-C contributed 5.64%, 5.98%, 4.54% and 6.08% respectively for Station 1, Station 2, Station 3 and Station R and PP-C contributed 2.22%, 3.31%, 2.46% and 3.09% respectively to the total percentage of POC. Together the contribution of these compounds to the total POC varied from 2.27% to 17.78%, 2.02% to 14.52%, 2.51% to 11.69% and 1.16% to 20.83% with means 7.86%, 9.3%, 7%, 9.17% respectively for Station 1, Station 2, Station 3 and Station R. Their contribution to POC was high for Station 2. The high contribution of PCHO and PP to POC may result from a predominantly autochthonous input of organic matter, for example from in situ primary production (Thurman, 1986). It was interesting to note that the organic matter collected showed some enrichment of proteins and carbohydrates during monsoon. The relatively higher protein and carbohydrates concentration during monsoon may reflect selective partitioning of dissolved organic material between water and

negatively charged particles, such as clay minerals (Hedges et al., 1994). Basic amino acids and/or other nitrogenous compounds impart a positive charge on dissolved organic materials such as proteins and humic acids within the natural pH (Thurman, 1986; Hedges et al., 1994). Such a process may have facilitated the adsorption of protein on clay minerals and other particles, thereby enhancing the protein content of the TSS material after the rain. Further, the observed increase may also be due to the adsorption or colonization of bacteria and/or diatom onto the clay minerals. During premonsoon and postmonsoon the contribution of these compounds to the total POC were very poor, which indicates the presence of extensively degraded organic matter. The contribution of carbohydrate and protein to POC increased during monsoon implying a relative abundance of fresh biogenic organic matter, which might be due to increased surface run-off. Alternatively, the decrease in PCHO-C plus PP-C contribution to POC may be due to dilution by inorganic material. The latter seems possible at Station 1 and Station R because of the slight inverse relationship between the PCHO-C plus PP-C/POC (%) and the concentration of TSS (-0.695 and -0.684). Station 2 and Station 3 showed a strong correlation between (PCHO-C plus PP-C)/POC (%) and the concentration of TSS (0.996 and 0.898). The contribution of these compounds to POC decreased with the increase in SPM content of the water at Station 1 and Station R, but showed a reverse at the other two Stations. This difference in relationship between the nature of POC and TSS concentrations for different Stations may be either due to differences in the sources of organic matter or due to biodegradation processes.

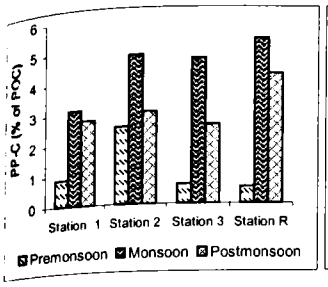

Figure 5.12:- Spatial and seasonal variation of particulate protein carbon as percentage of organic carbon

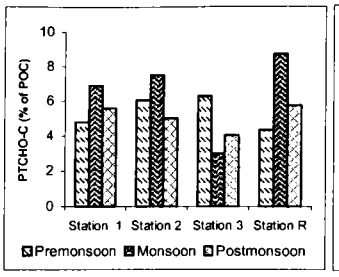

Figure 5.13:- Spatial and seasonal variation of particulate carbohydrate carbon as percentage of organic carbon

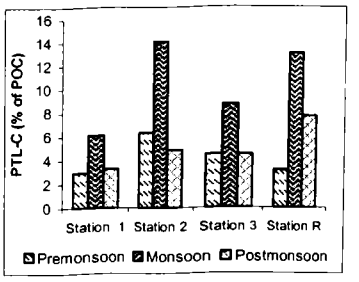

Figure 5.14:- Spatial and seasonal variation of particulate lipid carbon as percentage of organic carbon

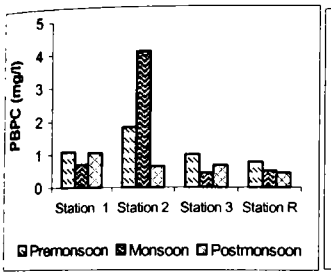

Figure 5.15:- Spatial and seasonal variation of particulate biopolymeric carbon

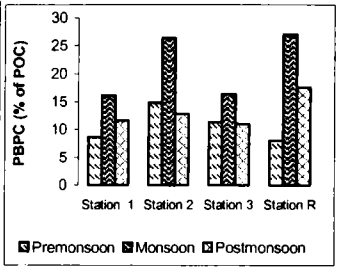

Figure 5.16:- Spatial and seasonal variation of particulate biopolymeric carbon as percentage of organic carbon

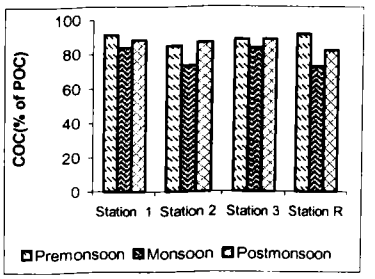

Figure 5.17:- Spatial and seasonal variation of particulate complex organic carbon as percentage of organic carbon

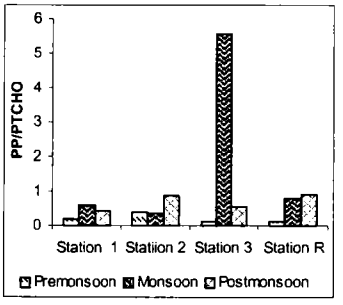

Figure 5.18:- Spatial and seasonal variation of particulate protein to carbohydrate ratio

The annual means for particulate biopolymeric carbon (PBPC) for the four Stations were 0.968mg/l, 1.89mg/l, 0.717mg/l and 0.585mg/l at Stations 1, 2, 3 and R respectively (Table A.31; Fig. 5.15). Mean PBPC% were 11.73%, 16.93%, 12.52% and 16.66% at Stations 1, 2, 3 and R respectively with annual ranges 1.28% (Station R, March) – 41.63% (Station R, July) (Table A.32; Fig.5.16). Station 3 which had a lower PBPC concentration than Station 1 showed higher nutritional quality than Station 1. Similarly Station R particulate matter was of

higher nutritional quality than Station 3, though it contains the lowest PBPC content than Station 3. Thus, although large amounts of particulate organic matter were recorded in Cochin mangrove area, this was of low nutritional quality.

The BPC was enriched with carbohydrates (51.23% and 45.06%) at Station 1 and Station R, followed by lipids; but for Station 2 and Station 3, the lipids were the major fraction (43.63% and 40.42%). BPC showed low protein content in all the four Stations (16.2%, 16.18%, 18.54% and 15.19%). During monsoon all the three components of PBPC were at their maximum in all the four Stations. BPC% was high during monsoon in all the four Stations. Particulate organic matter was therefore mostly composed of refractory material during premonsoon and postmonsoon that was largely unavailable to consumers.

The temporal pattern of organic matter composition in particulate matter showed an inverse relationship between amounts of organic matter and its potential availability to consumers: low quantities of high-quality organic matter (POC = 1.25mg/l; BPC% = 41.62%) at Station R in July were replaced by large quantities of (POC = 38.28mg/l; BPC = 1.28%) of low quality (high refractory material) at Station 2, September.

The results indicate that high nutritional quality is often not associated with high organic matter content. Station 3 was low in particulate organic matter, but its nutritional quality was comparable to other areas. Station 3 values showed recently produced organic matter. Although large amounts of particulate organic matter were recorded in Cochin mangrove area, they were of low nutritional quality. Food quality was better during monsoon. The results of the present study indicates that mangrove litter both within the system and those exported to the adjacent estuaries is highly refractory and of poor nutritional quality.

5.3.2 Degradation of Organic Matter

The residual and uncharacterised fraction of the organic carbon is defined here as complex organic carbon (COC) which is determined as the difference between total organic carbon and biopolymeric carbon and accounts on a mean 88.27%, 83.07%, 87.48% and 83.34% at Stations 1, 2, 3 and R respectively (Table A.33; Fig. 5.17). Thus a significant fraction of the organic carbon were of less degradable nature, which may be due to the transport of this component from the

sediment to the water column by the action of tides, waves etc. These findings confirm the high amount of COC present in the mangrove area. A decrease in labile POM is found when the concentration of suspended matter is high. This is probably due to the decreased light penetration in highly turbid waters, which decreases primary production resulting in a low contribution of labile POC (Ittekkot and Arain,1986). Ittekkot and Laane (undated) showed that the TSS concentration in the range between 1 and 150 mg/l had a mean labile content of about 35%, whereas at concentrations above 150 mg/l the labile content drops to about 15%. The major trend is a decrease in the percentage of POM with logarithmically increasing concentrations of suspended matter Meybeck (1982). This could be a consequence of a reduction in primary production due to high suspended matter concentrations (Thurman 1985).

Studies on other aquatic systems also reported that large amounts of refractory or degraded POC were associated with high sediment loads during high river discharge in the Indus River (Ittekot and Arain, 1986). Relative amounts of labile and residual organic fractions were found to vary between rivers on an annual basis. Temperate rivers such as the Mackenzie, St.Lawrence and Parana were reported to contain 35-40% labile POC, whereas for the Ganges, Brahmaputra, Indus and Orinoco only 20-25% of the total POC was described as labile (Ittekkot, 1988). Kristensen et al., (1992, 1995) also reported that mangrove soils are rich in organic matter, but the detritus is relatively nutrient poor and refractory resulting in low net mineralization rates.

The contribution of PCHO-C plus protein-C to the POC is also a potentially useful to evaluate the degradative state of organic matter (Ittekkot and Arain, 1986; Cowie and Hedges, 1984; Hedges et al., 1994; Cowie et al., 1995; Hernes et al., 1996; Opsahl and Benner, 1999). Carbohydrates and proteins account for 30 to 70% of the organic matter in all types of fresh marine and terrestrial sources, which appear to decrease during early degradation in the water column and newly deposited sediments (Cowie and Hedges, 1994; Cowie et al., 1995; Pantoja and Lee, 1999). It has been suggested that the decrease in the relative contribution of carbohydrate and protein (i.e. labile organic carbon) to organic carbon may reflect the nature of organic matter (Cowie and Hedges, 1994; Cowie et al., 1995). Therefore, the relative contribution from these two compound classes to the total

POC may reflect the degree to which the biodegradation of organic matter has proceeded. Conversely, the contribution of PCHO-C plus PP-C to the total POC indicates the potential of degradation of organic matter within the water column. As compared to the live material, the observed values were low, suggesting the degradation of organic matter and/or dilution by PCHO and PP poor organic or inorganic material.

The neutral sugar profile provides additional indicators of degradative state of organic matter (Hedges et al., 1994; Hernes et al., 1996; Opsahl and Benner, 1999). For example, glucose content (as weight percentage) is another factor that indicates the degradative state of organic matter. Glucose contributes 58 to 90% to the total PTCHO in fresh plankton and terrestrial tissues (Cowie and Hedges, 1984; Opsahl and Benner, 1999). Hernes et al. (1996) suggested that a high glucose content of particulate organic material indicates a diagenetically less altered stage. Rather than using individual neutral sugars, the neutral sugar yield (contribution of neutral sugar carbon to organic carbon) may be an alternative as a robust indicator for organic matter reactivity, with higher indicating fresher, less degraded material (Skoog and Benner, 1997; Amon et al., 2001). Due to preferential utilization, weight percentages of glucose tend to decrease from marine planktonic source to benthic sediments (Hernes et al., 1996; Jennerjahn and Ittekkot, 1999). Similarly, a decreasing trend for weight percentage glucose has also been reported for the highly degraded terrestrial plant material (Hedges et al., 1994; Opsahl and Benner, 1999). For Station 1 and Station R the monosaccharide percentage of total carbohydrates were very high 53% and 60.5% and for Station 2 and Station 3 contributions were 45% and 42% respectively.

Protein to carbohydrate (PP:PTCHO) ratio is also assumed to be an estimate of organic material ageing (Fabiano et al., 1997). Since proteins are more readily utilized by bacteria than carbohydrates (Newell and Field, 1983; Ianni et al., 2000) and are rapidly bound into refractory compounds, low values of PP:PTCHO ratio suggest the presence of aged organic matter (Danovaro et al., 1993) and a role of labile proteins as a potentially limiting factor for consumers (Jumars and Wheat croft, 1989; Fabiano et al., 1995). The PP:PTCHO ratios (Table A.34; Fig. 5.18) potrayed very wide variations (0.393, 0.596, 1.674 and 0.557 for Stations 1, 2, 3 and R). PP:PTCHO ratio reached 14.9 at Station 3 in August'00 indicating the presence of

newly-produced matter. This is because of the fact that at this Station the tidal effect is a maximum and this readily scavenges the organic matter as soon as it is formed. This indicates organic matter at Station 3 in August'00 (during monsoon) was of recent origin (excretions, dead organisms, fresh detritus etc.), because bacteria use the proteins more rapidly than the carbohydrates (Ianni et al., 2000). Conversely, for the rest of the study period especially during premonsoon, PP:PTCHO ratio remained below 1, confirming that the mangroves were characterized, for most part of the year, by a large amount of aged and/or non-living organic matter. These values were comparable to those observed in the Arno estuary (PP:PTCHO = 0.3 to 3.6; Fabiano and Dano-varo, 1994) and to those reported from the Ligurian Sea (PP:PTCHO = 0.14; Fabiano et al., 1995) and from Eastern Mediterranean Sea (PP:PTCHO = 0.09; Danovaro et al., 1993). In a similar study by D'Souza and Bhosle, (2001) on carbohydrates in suspended particulate matter in the Dona Paula Bay (west of India), PP/PTCHO varied between 0.56 to 3.18.

5.4 SUMMARY

Results of the present study illustrates the complexity and vast range of particulate organic matter constituents in mangrove waters. Despite these, results indicate that (POM) is a major component in mangrove ecosystems. Analyses of each POM fraction indicates that in mangrove ecosystem highly labile fractions like monosaccharides and free amino acids are present in low quantities, whereas refractory compounds dominated the organic matter composition. Thus the mangrove ecosystems, though containing a high organic matter load is of poor nutritional quality and of less labile nature. All the mangrove Stations contain high POC concentration compared to the estuarine Station. Of the three mangrove Stations, Station 2 was rich in organic matter due to high mangrove plant density and its isolated condition with low tidal flushing. Station 3 showed low organic matter content may be because of high tidal activity and dilution by fresh water discharge. But the biopolymeric carbon percentage of this Station was comparable to that of other two-mangrove sites indicating that Station 3 contains low quantity organic matter with moderately good nutritional quality. Thus the food quality of the three mangrove stations were more or less in the same range. Eventhough

mangroves produce large amount of organic matter, the nutritional quality of organic matter was more or less similar to that of estuarine reference Station.

POM showed no specific seasonal and diurnal variation, but showed significant spatial variation. This could be attributed to difference in amount of organic matter input, tidal activity, geographical settings etc.

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Chapter 6

SEDIMENTARY ORGANIC MATTER

6.1 INTRODUCTION

Mangroves are the dominant ecosystems modifying the physical and biogeochemical properties of intertidal sediments along many of the world's subtropical and tropical coastlines. Despite the importance of mangroves in coastal food chains, in stabilizing the shorelines, and as nutrient filters, their impact on sediment biochemistry is poorly understood. Sediments are indicators of the quality of overlying water and its study is a useful tool in the assessment of the status of environmental pollution. An understanding of mangrove sediment relations is crucial because such interactions are likely to be important to be regulating tidal water flow, sediment transport and element cycling within mangrove waterways, and between mangroves and adjacent coastal waters (Alongi 1998; 2001). A comparison of functional similarities and differences among mangrove forests in various coastal settings would provide valuable clues as to the importance of the role of these ecosystems in coastal biochemical process.

6.2 ORGANIC MATTER IN MANGROVE SEDIMENTS

Several reports have been made on the chemical and geochemical studies of the Cochin estuary. However, the composition of organic constituents in Cochin mangrove sediment has not been studied in detail. The present study deals with the horizontal as well as the vertical distribution pattern of sediment organic carbon in the intertidal areas of Cochin mangroves.

The organic matter content in the mangrove sediments is often higher than that in estuarine sediments due to the inherent biological productivity within the mangrove systems. Decomposition of the mangrove foliage and other vegetative remains and their resuspension contribute substantially to the organic matter content in the mangrove sediments. Planktonic material and macrophyte detritus are usually deposited in a relatively fresh and labile form at the oxic sediment-water interface. The infaunal density and diversity is particularly low within the mangrove forest, whereas burrowing crabs are the dominating faunal feature. These may, however, handle and consume a considerable fraction of the litter fall (Kristensen et al., 2000). A large fraction of organic matter deposited on sediment surfaces is degraded and remineralized by early diagenetic processes near the sediment-water interface

(Henrichs, 1992). The degradation is mediated by an array of aerobic and anaerobic microbial processes in the dynamic interface with a concurrent release of inorganic nutrients using oxygen as an electron acceptor. Several factors are believed to control reaction rates in surface sediments, including organic matter quality (i.e., the chemical composition), age (i.e., decomposition stage), particle associations (i.e., sorption to mineral surfaces, organic matrices, clay lattice structures and micropores), bioturbation (i.e., physical disturbance and macrofaunal consumption) and environmental conditions (i.e., temperature and the concentration of O_2 and other electron acceptors) (Mayer, 1994a,b; Keil et al., 1994; Fenchel et al., 1998). All these processes influence the vital activity of aquatic organisms by either facilitating or suppressing the respiratory and nutritive systems.

6.2.1 Surface Sediments

- ***Sedimentary Organic Carbon (SOC)***

The level of organic carbon in sediments is reported to be a reliable index of nutrient regeneration and the productivity of a water body. The carbon and nutrient cycles in mangroves are temporarily and spatially highly variable since they are regulated by a variety of factors such as soil type and texture, tidal range and elevation, redox state, bioturbation intensity, forest type, temperature and rainfall (Kristensen et al., 1991; 1992; Alongi et al., 1992; 1993; Woodroffe, 1992; Robertson et al., 1992). As the preservation and burial of organic matter in aquatic environments is a function of the rate of primary productivity, water depth, dissolved oxygen content in the water column, sedimentation rate, biological activity, and sediment stability, the organic carbon contents of sediments can be a sensitive indicator of the nature of source areas and the environments of deposition (Emerson and Hedges, 1988). Long-term burial of organic matter has been a key process in the formation and maintenance of an oxygen rich atmosphere (Berner, 2001), be its burial of terrestrial plants in fresh water swamps leading to extensive coal formation (Holland, 1987) or the deposition of organic matter in marine deposits (de Haas et al., 2002). Whether the coastal systems act as net carbon sources or as sinks remains debatable, largely because coastal systems vary substantially in response to external change (Hung and Kuo, 2001).

The primary purpose of this investigation was, therefore, to determine the distribution of organic carbon and the extent to which this distribution is related to other factors, such as primary productivity, oxygen content, bottom topography, and hydrodynamic features. Total organic carbon of the sediment has a major role in keeping the fertility of soil and thereby augmenting the biological productivity. Since the mangrove ecosystem is one of the most productive aquatic ecosystems like coral reef and sea grass, an understanding of its organic carbon is pre-requisite for assessing and also determining the extent of nutrient input into the surrounding mangrove water.

The results obtained for SOC in the present study are furnished in Table A.35 and the seasonal variation is depicted in the Fig. 6.1. Peak SOC concentration (152.76mg/g) was very clear in September'00 at Station 2. The lowest concentration (9.83mg/g) was observed in May'00 at Station 3. The annual mean values for the three stations were 71.46mg/g, 87.92mg/g and 32.97mg/g for Station 1, 2 and 3 respectively.

Seasonal variation showed a minimum at Station 3 during pre-monsoon and maximum at Station 2 during monsoon. The trend Station 2 > Station 1 > Station 3 was observed during all the three seasons, ie., the sediments of Station 3 was poor in carbon and that of Station 2 was richer.

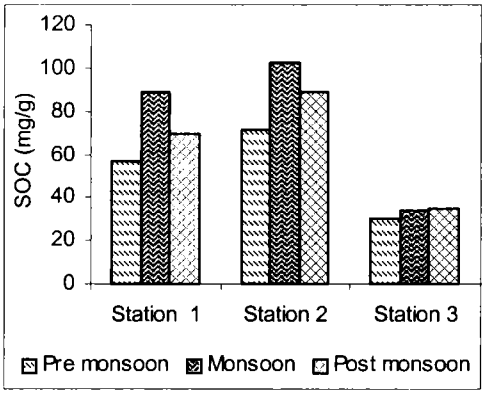


Figure 6.1: Spatial and seasonal variation of organic carbon in surface sediments.

The SOC content at the three stations during three seasons exhibited wide fluctuations in their concentration as evidenced by the ANOVA (Table B.7).

The hydrology of the Cochin mangrove system is regulated mainly by high rainfall during the monsoon and by tidal inundation. There are both physical and biological factors associated with decaying mangrove litter but biological factors seem to be more important than physical factors. Litter decomposition was recorded as being higher in brackishwater than freshwater (Herald, 1971) or in seawater (Boonruang, 1978). Moreover, decomposition is facilitated in low salinity and aerobic conditions (Mall et al., 1991).

Sediments from Stations 1 and 2 had significantly high levels of organic carbon when compared to other mangrove areas. The high levels organic carbon in mangrove sediments are due to decomposition of dead organisms, decomposition of mangrove detritus and anthropogenic inputs, particularly oil spills, sewage etc. which are transported by tides and strand on low energy ecosystems such as mangrove forests. Microbial degradation of the high content of organic matter in mangrove sediments generally removes all oxygen from sediments below the surface layer, creating ideal conditions for bacterial sulphate reduction (Berner, 1983). The production of hydrogen sulphide resulting from decomposition of organic materials decreased the pH value in mangrove sediments. Sediment samples, especially from Station 2 were often anaerobic and had a pronounced smell of hydrogen sulphide. Textural studies revealed that, silt and clay together constitute the predominant fraction at Stations 1 and 2 whereas the sand fraction was predominant at Station 3 (Fig. 6.14a-c). Organic carbon values of the sediments were higher at Station 2 compared to other stations. Association of organic matter with fine-grained sediment is well established (Bijoy Nandan and Abdul Azis, 1996; Nair et al., 1993; Sarala Devi et al., 1995). One of the features of organic carbon in the sediments is its inverse relationship with particle size of the sediments. This is observed from their positive relationship with silt and clay fraction and inverse correlation with sand fraction (Table C.11a-c). The finer fractions showed an efficacious relationship with organic carbon while the coarser fractions have no patent kinship (Sunilkumar, 1996).

The variation observed between stations can also be attributed to difference in mangrove species inhabiting the area. Station 1 is dominated by *Acanthus Ilicifolis, Rhizophora apiculata, Rhizophora mucronata, Excoeacaria agallocha, and two mangrove associates Clerodendronica and Acrostica. Whereas, Avicennia officinalis*

and *Bruggeria Gymnorhiza* inhabited Station 2. Station 3 was inhabited with *Acanthus Ilicifolis* and *Avicennia officinalis*. Significant differences in sulphide content, acidity, total organic matter content and trace metals and redox potential exist between soils colonized by different mangrove species, in particular between *Avicennia* and *Rhizopora* soils (Lacerda et al., 1993;1995). Most of these differences have been attributed to the different capacity of a given mangrove species to alter soil condition adjacent to its root systems through specific physiological mechanisms such as releasing oxygen into the reducing soils (Nickerson and Thibodeau, 1985). However, different soil conditions can also result from differences in the composition of initial organic inputs from mangrove litter, since mangrove leaves are compositionally complex and their early diagenesis is a selective process, resulting in changes in composition over time (Benner et al., 1990b). *Rhizophora mangle* leaves are very rich in tannin (Lacerda et al., 1995) and these substances have been reported to decrease the activity of benthic organisms in *Rhizophora*-dominated mangrove forests (Alongi et al., 1989).

Changes in organic carbon content of sediment with respect to seasons were observed at all the three stations. Organic carbon was highest during the postmonsoon period. This may be due to the low water condition caused by the construction of barriers during monsoon and postmonsoon to prevent the loss of prawn seeds. The low tidal activity, during monsoon and postmonsoon resulted in the development of a stagnant condition in the mangroves at Station 2 leading to a sharp rise in the organic carbon content during these seasons. But during premonsoon, the area was open to tidal access and the tidal flushing not favorable for the accumulation of organic matter in sediments result in the removal of organic matter from the system during the ebb. This difference in tidal activity can be observed in the difference in texture in these seasons also (Fig. 6.14a-c). The variation in texture is attributed to the influence of tides and monsoonal floods. Sand percentage was a maximum during premonsoon and least during monsoon. It is mainly due to the tidal action which removes the finer particles allowing coarser particles to be deposited (Mohan, 2000). The clay requires quite conditions for its deposition and such a situation is conducive for flocculation and settling of finer fractions. Cycling of organic matter in coastal environments often exhibits pronounced seasonal variations. Fluctuations in benthic metabolism, nutrient

regeneration and sediment–water interactions are usually considered a response to the annual variations in water temperatures (Kristensen 1993). Diagenetic analysis of newly deposited sediments have shown that the quality as well as the quantity of sedimentary organic carbon controls microbial processes (Burdige 1991; Kristensen and Hansen 1995).

Previous work done by Shriadah (2000) on the distribution of organic carbon contents of sediments along the Arabian Gulf shoreline of the U.A.E. showed a range from 1.8mg/g to 22.5mg/g. Higher values were mainly attributed to the decomposition of mangrove detritus, decomposition of dead organisms. Nasnolkar et al. (1996) showed that the sediment organic carbon content varied from 1.04 to 32.77mg/g in the sediments of Mandovi estuary, Goa. Hoq et al. (2002) reported that the organic carbon ranged between 12.2mg/g and 15.1 mg/g in sediments of Sundarbans mangrove, Bangladesh. The organic carbon in the sediments of mangrove and estuarine ecosystems of Goa, ranged from 1.03% to 5.41% (Sardessai, 1993). Padma and Periakali (1999) observed organic carbon in the sediments of Pulicat Lake to be more during postmonsoon (113mg/g),due to the riverine input and heavy rainfall. Anila Kumary et al. (2001) observed organic carbon variation in estuarine sediments of Poonthura (southwest coast of India) from 2.5 to 84 mg/g. Badarudeen (1997) reported that the organic carbon of Kochi mangroves, ranged between 5.2mg/g and 48.9mg/g with a mean value of 26.2mg/g. In the same study, sediment cores of Vypin showed a mean value of 69.8mg/g (64mg/g to 79.4mg/g) for organic carbon content. In Gundu island, Elamkulam and Maradu, Sunil Kumar (1996) found spatial variations of organic carbon ranging from 1.7 to 11.7mg/g, 12.3 to 29.7mg/g, and 3.5 to 40.5mg/g. Investigations done by Joseph and Chandrika (2000) in mangrove swamps of Cochin confirmed the values reported by Sunil Kumar (1996) and reported organic carbon content variation between 9.5mg/g and 41.8mg/g. In a study by Ramanathan et al. (1999) in Pichavaram mangrove sediments organic matter concentration varied from 25mg/g to 134mg/g.

Values obtained for SOC in the present study were slightly higher than those reported earlier, especially those at Station 1 and Station 2. This might be due to the clayey-silt nature of the sediments of the study area. As a rule, sedimentary organic matter in mangroves is morphologically and geochemically poorly

preserved while the SOC contents, ranging from 17 to 48%, in mangrove sediments of Guadeloupe, French West Indies are among the highest values described in such environments, due to the stagnant conditions of the ecosystem (Lallier-Verges et al., 1998). Many authors found the organic content of mangrove sediments to be usually high, with carbon levels typically ranging from 2 to 15% i.e., 20 to 150mg/g dw (Boto and Wellington, 1984; Kristensen et al., 1988; 1995).

Several studies on organic carbon balance in mangrove forests have indicated that these intertidal ecosystems are a sink for carbon, despite some evidence for limited export of plant litter (Robertson et al., 1992; Kristensen et al., 1995; Alongi et al., 1999). These studies indicate that most of the carbon is vested in above and below-ground biomass and stored in sediments. Intense bioturbation, dilution of porewater by monsoon rains, poor nutritional quality of organic matter, translocation of oxygen via dense roots and rhizomes, and tidally-induced oscillation in redox status, are considered prime factors regulating microbial decomposition (Alongi, 2001).

➢ ***Sedimentary Organic Nitrogen (SON)***

Nitrogen enters mangrove sediments primarily via autochthonously produced leaf litter, microalgae, and epiphytes. Other sources include nitrogen fixation by bacteria as well as import of particulate and dissolved nitrogen from the adjacent coastal zone (Alongi et al., 1992).

The organic nitrogenous compounds produced from the degradation of organic matter gets adsorbed onto sediments depending upon the temperature, electrical conductivity of the interstitial water, the concentration of organic matter and porosity of sediments (Nasnolkar et al., 1996). Due to the high content of nitrogen-deficient structural carbohydrates in mangrove litter entering the sediment, the nitrogen content of sediment detritus is relatively low, ranging from 0.05 to 0.4% dw (Kristensen et al.,1991; 1995; Alongi et al., 1992). During senescence of the leaves, i.e. before litterfall, about 64% of the nitrogen is resorbed by the mangroves (Rao et al., 1994). Consequently, the sediment receives mangrove material that is strongly depleted in nitrogen with respect to fresh mangrove leaves.

Nitrogen fixation by cyanobacteria and heterotrophic bacteria, which is the best-studied nitrogen transformation process in mangrove systems, occurs on all inhabitable surfaces within the system: sediment surface, prop roots, pneumatophores, roots, bark, logs, and leaf litter (e.g. Alongi et al., 1992). Nitrogen mineralization or ammonification, where nitrogen is liberated from organic matter in the form of ammonium via hydrolyzation and catabolization of proteins and polynucleotides, is mediated by nearly all heterotrophic organisms ranging from bacteria to macrofauna (Kristensen et al., 1995). Both benthic microalgae and bacteria are responsible for a very rapid turnover of nitrogen in mangrove sediment (Kristensen et al., 1995). As suggested by Alongi (1989b), bacteria (and benthic microalgae) in mangrove sediments are sinks for nutrients because the system is characterized by a closed internal recycling - death, decay, uptake, growth - and thus serve as a mechanism for nutrient conservation (i.e. reducing net system mineralization). Eventually nothing is known about the role of crabs on nitrogen dynamics in mangrove forests. Although ammonium excretion by crabs must occur, the rates are presumably low due to the poor food (low nitrogen) quality (Alongi et al., 1992). However, while crabs remove carbon from the mangrove system as carbon dioxide via respiration, all nitrogen turned over by crabs eventually ends up in the sediment, either in the form of faeces, excretion products or carcasses (Kristensen et al., 1995).

In previous studies, the annual mean value of organic nitrogen compounds on the continental shelf of the Gulf of Lions (northwestern Mediterranean) was reported to be 0.049%.(Buscail et al., 1995). Total nitrogen ranged between 1.1 to 1.3 mg/g in sediments of Sundarbans mangrove, Bangladesh (Hoq et al., 2002). Organic nitrogen in the sediments of Harbour and Coastal areas of Visakhapatnam, East coast of India, varied from 0.68mg/g (0.068%) to 15.2mg/g (1.52%) (Sathyanarayana et al., 1994). The organic nitrogen in the shelf and slope sediment samples from the Arabian sea were 23.6mg/g to 56mg/g and that from a coastal sediment sample in the Bay of Bengal was 3.3mg/g (Sardessai, 1999).

Annual mean values of SON during the present study were 3.41mg/g, 4.58mg/g and 1.56mg/g at Stations 1, 2 and 3 respectively. Overall data (Table A.36 and Fig 6.2) showed the SON values ranging from a minimum of 1.27mg/g to maximum of 4.91mg/g. Higher organic nitrogen content at Station 1 and Station 2

may be attributed to restricted water circulation, texture type and geomorphology conducive to greater input and retention of mangrove- and macroalgae-derived detritus (Alongi et al., 1996). Low SON values at the Station 3 may be due to utilization of nitrogenous compounds, high tidal flush out, sandy texture and lower nitrogen fixation, (Vinithkumar, 1999). In general, the major source of nitrogen in sediment was attributed to the nitrogen fixation by benthic algal communities, which are strongly influencing the nitrogen budget (Vinithkumar, 1999).

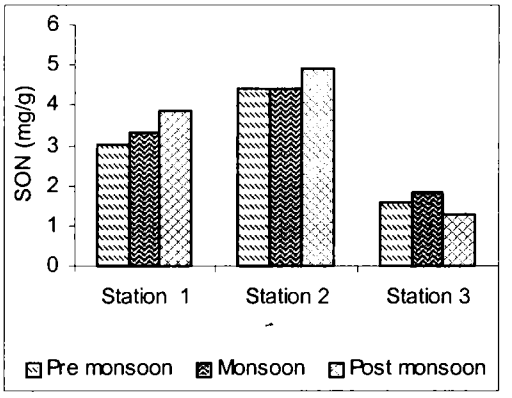


Figure 6.2: Spatial and seasonal variation of organic nitrogen in surface sediments.

SON exhibited no significant seasonal variation during the study period, which was also confirmed by the ANOVA (Table B.7).

SON showed negative correlation with salinity ($r = -0.42$; $P<0.05$) and SOC and with almost all other organic constituents (Table C.11a-c). This could be due to the utilization of salt minerals such as sodium, potassium and other organic compounds from sediments by the mangrove communities during their growth (Vinithkumar, 1999).

- ***Carbon/Nitrogen Ratio (C/N)***

The carbon and nitrogen cycles in the sea are inextricably linked to each other through production and mineralization processes (Biddanda and Benner, 1997). Sedimentary organic matter was depleted in carbon compared with fresh litter fall, as shown by the low C/N ratio of 18 compared with 70 for leaf litter (Dittmar and Lara, 2001). Senescent mangrove leaves of *A.officinalis* and *E.agallocha* have C/N ratios approximating 75. During decomposition, C/N ratios

decrease as a result of nitrogen enrichment, and lowest values reached are 31 for *Avicennia* and 24 for *Excoecaria* (Dehairs et al., 2000).This indicates selective loss of carbon due to leaching or respiration. Dittmar and Lara (2001) suggested that a rapid initial release of carbon and an enrichment of nitrogen during early degradation of leaf litter occurs, before its incorporation into the sedimentary matrix. The subsequent organic matter degradation in the sediment is probably characterized by reduced mineralization rates and similar reactivities for carbon and nitrogen as evident for almost invariant C/N ratios in the sediment. To obtain this low C/N ratio in the sediment purely through depletion of carbon from the leaf letter, a rapid initial loss of ~75% of carbon from the litter because of mineralization or leaching would be necessary if other sources or sinks of carbon and nitrogen are excluded (Dittmar and Lara, 2001). The generally low C/N ratio suggests that the woody tissue did not contribute substantially to the sedimentary organic matter in general. The influence of decaying material was probably limited to the proximity of dead woody tissue, as in the case of the decomposed root that caused local maxima of C/N and organic carbon (Dittmar and Lara, 2001). During subsequent decomposition and bacterial colonization, however, nitrogen enrichment occurs through nitrogen fixation (Woitchik et al., 1997) and immobilization, both on the forest floor (Twilley et al. 1992) and in the water column (Cifuentes et al., 1996). These processes result in much lower C:N ratios for mangrove detritus (Bouillon et al., 2000). For comparison, organic matter in most subtidal marine sediments supported predominantly by algal detritus has a C:N ratio around 10 (Kristensen et al.,1995). Materials rich in nitrogen, such as microalgae with low C:N, favor net bacterial mineralization, whereas those poor in nitrogen, such as mangrove leaves and wood with high C:N, favor net bacterial immobilization (Kristensen et al.,1995).

C/N ratios in the present study are given in Table A.37 and the seasonal variations are shown in the Fig. 6.3. Annual mean values of C/N at Station 1 was 21.1; at Station 2, 19.21 and that at Station 3 was 21.55. The low values during premonsoon may be due to increased benthic activity. Lower C/N at Station 2 may be attributed to increased rate of mineralisation due to restricted water circulation, high benthic fauna, geomorphology conducive to greater input and retention of mangrove- and macroalgae-derived detritus (Alongi et al., 1996). Station 3 showed

the highest value probably because of fresh organic matter with low rate of mineralisation. Mangrove detritus has high C:N ratios and a significant fraction of the organic matter is considered to be refractory humic compounds and geopolymers (Benner et al., 1990a; Kristensen et al., 1994). This is probably an important cause of the observed low rates of mineralization in mangrove ecosystems despite the ambient high temperatures (Kristensen et al., 1992, 1995; Holmer et al., 1999).

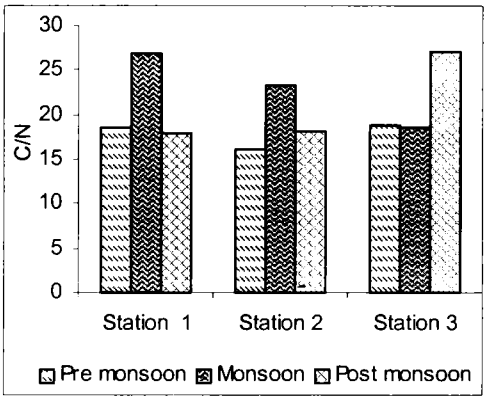


Figure 6.3: Spatial and seasonal variation of carbon/nitrogen ratio in surface sediments.

C/N ratio is generally used to identify the source of organic matter in sediments. In a similar study Buscail et al. (1995) on C/N on the continental shelf of the Gulf of Lions (northwestern Mediterranean), the annual mean value was 11.2. C/N ratios of sediments of Vellar estuary fluctuated widely between 4.25 and 137.5 and the changes were explained to be due, among other things, to the changing texture of the sediments and the content of wood and leaf debris that originated from the mangrove vegetation (Sivakumar et al., 1983). High values of C/N ratio were stated to be due to degradation of complex protein in the case of Arabian shelf sediments (C/N ratio = 2.48-37.5) (Bhosle et al., 1977) and to the input of fresh water humus into sediments in the case of Cochin backwater (2.5-16.9) (Sankarnaraynan. and Panampunnayil, 1979). The C/N ratios of sediments of Mandovi estuary, Goa, were 0.2 to 2.0 (Nasnolkar et al., 1996), those from the west coast of India (*R V Meteor*) had ratios of 1 to 8 and from the shelf sediments of the Arabian Sea with ratios of 2.48 to 37.5 and also of the sediments from the Cochin Backwaters (av. 6.4) (Qasim and Sankaranarayanan, 1972). C/N (atomic) 12 has

been attributed to the terrigenous material [Kukal, 1971] whereas C/N (atomic) 10 is considered as an indication of the marine nature of the organic matter [Parsons, 1971]. Boto and Bunt (1981) assumed that high C:N ratio values in intertidal sediments were related to mangrove export. The relatively high export during the rainy season from the forest to the flat was certainly the result of intensive rainfall, which drew the organic matter from the mangrove to the subtidal zone.

☞ ***Labile and Refractory Constituents***

As in the case of dissolved and particulate organic matter SOC and SON can be divided into labile and refractory constituents. The more labile organic matter is rapidly consumed by the intense biological benthic activity whereas, the refractory ones being resistant to microbial attack remain within the system and/or are exported to the neighboring ecosystems.

➢ ***Spatial and Temporal Variation of Sedimentary Labile Constituents***

- *Sedimentary Amino acids*

The primary organic nitrogen compounds in the biosphere are combined amino acids, which occur as enzymes, peptides and proteins in cells and extracellular products. Free amino acids are individual monomers formed by the hydrolysis of peptides and proteins from enzymes and bacterial activity, or as plankton intra- and extracellular products (Sigleo and Macko, 1985). Combined amino acids includes amino acids contained in proteins, but also those liberated from other geopolymers like polypeptides, peptides and bound amino acids found in particulate material.

In the present study a maximum (37.4mg/g) for total amino acids (STAA) was observed in the month of August'99 at Station 2. For free amino acids (SFAA), maximum (0.552mg/g) was found in March'00 for the same station, and for combined amino acids (SCAA) Station 2 showed the maximum (37.07mg/g) in August'99. The lowest concentrations of the three amino acids were found at Station 3 and were 4.42mg/g (April'00), 0.038mg/g (May'00) and 4.33mg/g (November'00). Tables A.38, A.39 and A.40 give the monthly variation of STAA, SFAA and SCAA respectively. Seasonal variations are shown in the Figures 6.4, 6.5 and 6.6 respectively.

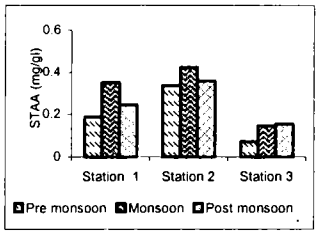


Figure 6.4: Spatial and seasonal variation of total amino acids in surface sediments.

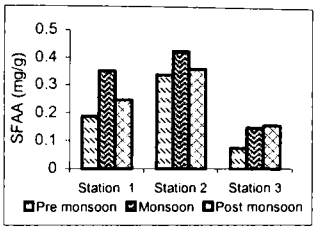


Figure 6.5: Spatial and seasonal variation of free amino acids in surface sediments.

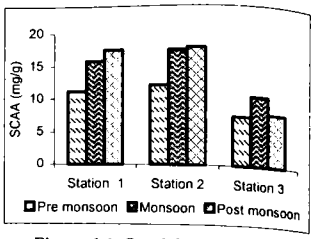


Figure 6.6: Spatial and seasonal variation of combined amino acids in surface sediments.

SCAA and STAA behaved almost conservatively to each other, it was because of the fact that SCAA contributes most of the STAA, only a negligible fraction has appeared as SFAA. The low concentration of SFAA was probably due to microbial utilization. SFAA were maintained at a low constant level because they were utilized by microbes very efficiently. All the three types of aminoacids showed their least value at Station 3 during all the three seasons throughout the study period. The concentration of Station 3 was very much low.

SFAA showed a maximum at Station 2 during monsoon and a minimum at Station 3 during premonsoon, showing an overall mean value of 0.22mg/g. Station 1 and Station 2 showed similar variation with maximum during monsoon and minimum during premonsoon. But at Station 3 the maximum was obtained during postmonsoon and minimum during premonsoon. Thus all the stations showed their minimum SFAA values during premonsoon. The annual mean values obtained for each station were 0.26mg/g, 0.372mg/g and 0.131mg/g.

Both STAA and SCAA exhibited their lowest values during premonsoon. The annual mean values of SCAA for the three stations were 15.25mg/g, 16.08mg/g and 8.51mg/g, the overall mean value was 12.58mg/g; and for STAA they were 15.51mg/g, 16.45mg/g and 8.64mg/g, with an overall mean value of 12.8mg/g. All the three forms of aminoacids showed the same trend with amino acid concentration being maximum at Station 2 and least at Station 3. Variability of soil parameters may be explained by physical factors such as tidal amplitude, inundation period, and soil granulometry (Lacerda et al., 1995). Higher values at Station 2 might be due to increased adsorption of amino acids by sediment. The higher adsorption in the sediment may be due to the high organic carbon content, and clay minerals, but also to the composition of the organic matter reaching the floor and the intensive

bioturbation, which may provide attractive sites for adsorption of amino acids by exposing new surfaces in the sediment (Wang and Lee, 1993; Jorgensen, 1996). It is well documented that large grain sediment particles are deficient in organic matter especially in total amino acids (Sardessai, 1999). In contrast, fine grain sediments exhibit organic matter enrichment. Evidently, clayey sediments contain adsorbed humic substances, which are bound to clay minerals by amino acids of proteins (Sardessai, 1999). Deamination of these complexes releases the humic materials from the clays (Wershaw and Pinckney, 1980).

At Station 1 significant negative correlation of SCAA and positive correlation of SFAA with organic carbon (Table C.10a) suggests that organic carbon is enriched in free amino acids with respect to combined amino acids. Negative correlation shown by polysaccharides and humic substances with SCAA and STAA suggests the preferential degradation of amino acids by chemical or microbial hydrolysis in presence of the polysaccharides and humic substances. SFAA showed positive correlation with monosaccharides which may be due to their same rate of formation and degradation. Proteins showed positive relationship with combined amino acids and total amino acids, which suggests combined amino acids at Station 1 is enriched with proteins. Similar relationship was shown at Station 2 (Table C.10b), but not at Station 3 (Table C.10c) which means that at Station 3 combined amino acids was also enriched with some other components also. Negative correlation of SCAA with humic substances was shown at Station 2 also. At Station 2, SFAA showed a positive correlation with tannin and lignin, which suggests their same source, mangrove. At Station 3, SFAA showed a positive correlation with organic carbon, which suggest adsorption of free amino acids on to organic particles and also points to the fact that organic carbon at Station 3 is enriched in free amino acids. All the three forms of amino acids showed significant positive correlation with clay percentage and negative relationship with sand content (Table C.11a-c).

Diagenesis and adsorption of amino acids seem to depend both on the input rate and quality of organic material (Wang and Lee, 1993). Low values at Station 3 might be due to the sandy nature of the sediment and also due to the high tidal flushing. ANOVA also revealed that there is significant difference between stations for all the three types of amino acids (Table B.7). The activity of benthos in the

sediment (including micro-, meio-, and macrofauna) varies depending on temperature, oxygen concentration and input of organic matter, and this may also alter the rates of mineralization (Klump and Martens, 1989).The sediment is well oxygenated and bioturbated by macrofauna throughout the year. The overlying water at the sampling site is well oxygenated throughout the year. Microbial activity in sediments at most sites is generally regulated by seasonal changes of input of organic matter, bottom water temperature and oxygen concentration (Landen and Hall, 1998). The uppermost part of the sediment involves a very dynamic system. Amino acids are intermediates in the degradation processes which always occur both in the oxygenated part of the sediment and in the anoxic layers. The adsorbed amino acids may act as buffer and desorb from the sediment solid phase when the concentration of DFAA decreases (Landen and Hall, 1998).

ANOVA showed that there is no significant difference between seasons (Table B.7). However among the three seasons, premonsoon values exhibited the least among all the three stations. This may be due to low organic matter content and increased sand percentage during this seasons decreasing the amount of aminoacids adsorbed to the sediment, thereby allowing them for easy microbial attack. Increased concentration during monsoon and postmonsoon may be due to increased organic matter load and clay minerals which provides fresh adsorption sites. Amino acids can be adsorbed to surfaces of sediment particles, including organic material, or be incorporated into humic substances. Amino acids adsorbed to a much greater extent to organic matter than to clay minerals in the sediment (Landen and Hall, 1998). Natural sedimentary organic matter is composed of a mixture of various compounds, providing a variety of adsorption sites on the organic coating at the sediment surfaces. Fresh organic matter might provide more attractive sites for amino acid adsorption than do older and more refractory material and mineral particles (Landen and Hall, 1998). It can be seen that highest concentrations of amino acids were found in the surface sediment, and the amount of amino acids is low during premonsoon when water temperature was higher. One possibility of the lower concentrations of DCAA during premonsoon may be a combination of the higher benthic activity (more amino acids were hydrolysed from peptides and proteins when degradation rates increased) and more intensive bioturbation, which changed the composition of the organic matter in the sediment

making easy access for amino acid degradation either chemically or microbially. This means that degradation of amino acids do not necessarily depend directly on bottom water temperature, but on other processes, which in turn are related to bottom water temperature like microbial activity, growth etc. All this makes the interpretation of the seasonal distribution pattern very complicated. One explanation as to why a more obvious seasonal variation of free amino acid distributions was not observed could be that the rate of consumption of amino acids increased with higher benthic activity: greater assimilation, greater degradation, and higher adsorption.

Normalizing each of the concentration of three forms of amino acids with carbon and nitrogen values, some interesting results became evident. STAA-C and SCAA-C(% of SOC) mean values for each stations were STAA (12.64%, 11.32%and 17.71%) and for SCAA (12.45%, 11.08% and 17.48%) at Stations 1, 2 and 3 respectively. Annual SFAA % mean values for each station were 0.185%, 0.238% and 0.236%. Thus contribution of all the three forms of amino acids to the total carbon pool is maximum at Station 3. Similarly, STAA contributes a mean value of 61.7% to total nitrogen pool at Station 1, 49.28% at Station 2 and 78.76% at Station 3. SCAA contributes 60.62%, 48.13% and 77.59% to the total nitrogen pool. And, finally for SFAA the contribution to the total nitrogen pool was 1.08%, 1.15% and 1.17% at Stations 1, 2 and 3 respectively. Contribution to the total nitrogen pool of the three forms of amino acids were maximum at Station 3, whereas Station 2 the least. This means that the organic matter at Station 3 is the least mineralised and the mineralisation efficiency of Station 2 is the maximum as observed from the low contribution to the organic carbon and organic nitrogen pools. This may be due to the high benthic activity, presence of polychaete fauna, crabs etc., restricted tidal flushing with high organic matter input. Whereas, at Station 3, the sediment is covered with water almost all the time, with continuous flushing by incoming tides removing the organic matter even before mineralisation can occur. The observed increase in the contribution of free amino acids to the soil C-org and N-org pools at Station 3 may therefore be due to the addition of free amino acid material via microbial conversion of other C- and N- rich organic matter as well as due to the preferential degradation of other easily oxidisable organic matter (Lacerda et al., 1995).

- *Sedimentary Proteins (SP)*

Protein and their constituent aminoacids are typically the most abundant substances in phytoplankton and mangrove litter, and represent an important source of carbon and nitrogen in aquatic systems. Both marine and riverine bacterio-fungal decomposers thrive to convert mangrove litter into consumable protein (Jadav and Chowdhury, 1985) which are subsequently consumed by invertebrates and which ultimately cater as food for fish population. Thus, the key factor of this highly productive ecosystem is the contribution of plant litter, which forms the primary energy source. The large amounts of protein in phytoplankton (upto 75% of the particulate nitrogen, Nguyen and Harvey, 1994) are rapidly recycled in the water column (Harvey et al., 1995). Preservation of amino acids and protein does, however, occur under some conditions. The preservation of organic matter in aquatic systems may be attributed to the presence of inherently refractory biomolecules, condensation reactions that make compounds refractory (Ishiwatari, 1992), and/or slower rates of decay under anoxic conditions (Cowie et al., 1995; Harvey et al., 1995). The processes which preserve protein are unclear. It has been suggested that protein adsorption to plant detritus may sterically protect peptide bonds from proteolytic bacterial exoenzymes (Samuelsson and Kirchman, 1990). In addition, during degradation proteins and polypeptides may undergo chemical transformations including shiffs-base condensation with sugars to become insoluble and resistant to enzymatic attack (Keil and Kirchman, 1993). Extracellular hydrolytic enzymes such as proteases may bind irreversibly with structural analogs (e.g. proteins which have undergone chemical modification), yielding a large, refractory molecule (Lee and Henrichs, 1993). Recent evidence suggests that one mechanism for preservation of labile organic matter, such as protein, may be through chemisorptive attachment to mineral surfaces (Keil et al., 1994) or sorption in the small pores of minerals (Mayer, 1994a.b), which presumably protects the covalent linkages of biomolecules from the hydrolytic action of enzymes.

In the present study, the highest protein concentration (22.6mg/g) was observed at Station 1 in December'99 and the lowest (0.284mg/g) at Station 3 in March (Table A.41). The annual mean values for each station were 9.45mg/g, 9.55mg/g and 5.17mg/g at Stations 1, 2 and 3 respectively.

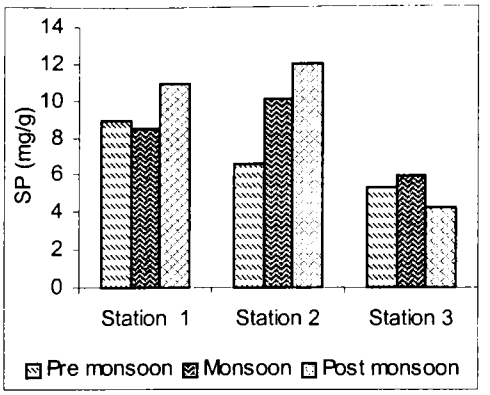


Figure 6.7: Spatial and seasonal variation of proteins in surface sediments.

Seasonal variation showed the highest protein concentration during monsoon and post-monsoon at Station 2 and lowest at Station 3 during pre-monsoon (Fig 6.7). Protein content of Station 3 was lower than the other two mangrove sites. The maximum obtained was at Station 2 in post-monsoon and minimum at Station 3 in post-monsoon. The low protein content at Station 3 may be due to low organic matter and high sandy nature of the sediment. High tidal activity at this site restricted the accumulation of proteins and were washed away with every incoming tide. Presence of high organic matter and clay content increased the amount of proteins at Station 1 and Station 2. Proteins are strongly adsorbed onto organic matter and clay minerals. Low tidal activity at Station 2 provides a suitable condition for the settling and adsorption of protein on to the surface sediments. Rhizophora apiculata plantations at Station 1 are highly efficient at sequestering labile carbon and nitrogen into plant biomass and sediment pools (Alongi et al., 2000). Nutrient cycling within mangrove sediment is dependent on many factors, including primary productivity, nutrient-use efficiency, nutrient resorption, sclerophylly, decomposition, nutritional quality of plant tissue, and allocation to defense. The efficiency of these plant-mediated processes depends on nutrient availability in the environment and inherent functional properties of plants (Feller et al., 1999). At Station 1, significant positive correlation of proteins with humic substances (Table C.10a) suggest that proteins take part in humification process and/or inhibitory effect of humic substances on degradation of proteins. Positive relationship with combined amino acids suggests that proteins comprise major part

of combined amino acid pool. At Station 2, a negative relationship was observed with humic substances (Table C.10b) which might be due to the preferential degradation of protein molecules with respect to humic substances. At Station 3, proteins showed a positive correlation with total lipids (Table C.10c), which might be due to their same rate of formation and degradation.

Significant difference between stations is confirmed by ANOVA. However, there is no significant difference between seasons (Table B.7).

Normalising with carbon and nitrogen, mean values of SP-C% of SOC for each stations were 7.79%, 6.29% and 7.45% (Table A.49) and that of SP-N% of SON were 44.39%, 33.16% and 52.97% at Stations 1, 2 and 3 respectively. Results of ANOVA showed revealed that the contribution of protein-nitrogen to the total nitrogen pool is significantly different between stations (Table B.9c). The least protein content of total nitrogen pool at Station 2 suggests the high rate of mineralisation due to restricted tidal influence, high organic matter input, high benthic activity due to low water condition. Presence of polychaete fauna was reported to be high at this station (Sunilkumar and Antony, 1994). The least observed at Station 2 may be due to the consumption of proteins by polychaete fauna, which together with the protein rich detritus, develops a detritus food web in the mangrove ecosystem which is mostly consumed by various estuarine and near shore shell and fin fishes. Marked seasonal variations in salinity influence the occurrence of polychaetes in the area, with premonsoon and postmonsoon showing the high species composition than the monsoon periods (Sunilkumar and Antony, 1994). Even though polychaetes were present at the three tidal levels, high population density was seen in the low tidal area and mid tidal levels. The canopy of the mangrove vegetation and the fine texture of the soil, provide a cool and stable environment quite favourable for the distribution of benthic organisms (Sunilkumar and Antony, 1994).

In the present study, proteins contributed 53.8% to 79.6% to the DCAA pool; the overall mean value being 61.9% and indicating that the major part of combined amino acids was in the form of labile proteins. Mean value of protein contribution to combined amino acids for each station were 65.2%, 59.9% and 60.7% at Stations 1, 2 and 3 respectively.

The bulk of organic nitrogen does not consist of proteins, even though proteins comprise 30-88% of living algal/vascular plant nitrogen (Cowie and Hedges, 1992). Ding and Henrichs (2002) by two-dimensional electrophoresis and amino acid analysis suggested that while most proteins are degraded during early diagenesis, a significant fraction be preserved. Small amounts of discrete proteins survive early diagenesis, with most proteins retained in the residual organic matter as extensively modified and cross-linked, acidic species. The adsorption and desorption of proteins and polyamino acids on illite, montmorillonite, goethite, and marine sediments was investigated by Ding and Henrichs (2002). The proteins were strongly and rapidly adsorbed by the clay minerals and sediments, and much of the adsorbed protein was not readily desorbed (Ding and Henrichs, 2002). Andrade (1985) described the non-covalent forces acting in the stabilization of protein structure in aqueous solution and on surfaces. These include ionic or electrostatic forces due to the attraction of two or more groups carrying opposite charges; hydrophobic interaction, which is basically an entropically driven process; hydrogen bonding, which is a dipole/dipole interaction with an associated energy change comparable to very weak covalent bonds; other interactions, which are usually dominated by Π–Π interactions. Montmorillonite adsorb the protein more strongly than illite. The apparent K values of the proteins were in the order of goethite ≥ montmorillonite >> illite reflecting the electrostatic properties of both proteins and minerals. Thus, proteins are strongly adsorbed by minerals and sediments. Electrostatic interactions between adsorbates and the particle surfaces, and between adsorbate molecules, are important in protein adsorption to minerals. The adsorption coefficient of the proteins are great enough to lead to their preservation in sediments.

There are many hypotheses that attempt to explain why bacteria do not remineralize all the organic matter present in sediments. Bacteria are pretty good decomposers, routinely consuming a large amount of the organic matter available to them in aquatic systems. However, some material escapes and are preserved in the sedimentary record. Organic matter left behind is either because some factors saved them or because they are really resisted to degrade. The quantity of protein delivered to sediments via the water column depends little on the redox conditions of the water column; anoxic and oxic water columns both deliver the same relative

quantity and quality of proteins to sediments, and its fate is to be essentially completely remineralized (Keil and Fogel, 2001). Most organic matter present in sediments is found in the form of aggregates that are surrounded by clay plates. There is a positive correlation between the proportion of clay-to-organic in the aggregates and the degradation state of the organic matter. Proteins in clay-rich aggregates are more fragmented and partially degraded than those in organic-rich aggregates (Arnarson and Keil, 2001; Keil et al., 2000; Van Mooy et al., 2002; Keil and Fogel, 2001).

- *Sedimentary Carbohydrates*

Carbohydrates, which include polyhydroxylated compounds ranging in size from 5-6 carbon sugars to large biopolymers (i.e., starches, cellulose etc.). Carbohydrates are much higher in vascular plants than in algae (Cowie and Hedges 1984). Carbohydrates, values were 0.37mg/g to 5.35mg/g in the harbour and coastal sediments of Visakhapatnam(Sarma and Rao, 1988). Lacerda et al. (1995) reported variation of carbohydrates in the core sediments of Avicennia soil in South-eastern Brazil from 1.41mg/g to 3.83mg/g and that of Rhizophora soil from 2.44mg/g to 2.50mg/g.

Similar to amino acids, Sedimentary Total Carbohydrates (STCHO) and Sedimentary Polysaccharides (SPCHO) behave almost similarly and the trend of Sedimentary Monosaccharides (SMCHO) was somewhat different. The Station 3 showed the lowest of all concentrations throughout the year for all the three types of carbohydrates. Monthly variations are given in Tables A.42, A.43 and A.44 and seasonal variations in Figures 6.8, 6.9 and 6.10 for STCHO, SMCHO and SPCHO respectively. The annual mean values for the three stations for all the three carbohydrates were as follows. For SMCHO the mean values were 0.609mg/g, 0.981mg/g and 0.310mg/g for Stations 1, 2 and 3 respectively. Similarly for SPCHO the values were 18.43mg/g, 15.45mg/g and 6.65mg/g for the three mangrove stations and for STCHO, they were 18.25mg/g, 15.89mg/g and 6.58mg/g for Stations 1, 2 and 3 respectively.

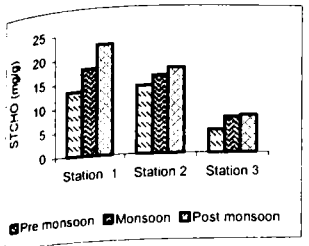


Figure 6.8: Spatial and seasonal variation of total carbohydrates in surface sediments.

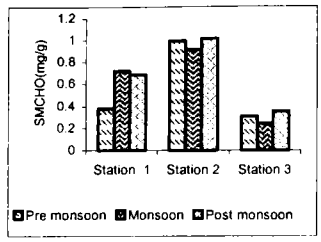


Figure 6.9: Spatial and seasonal variation of monosaccharides in surface sediments.

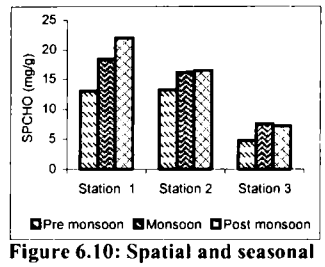


Figure 6.10: Spatial and seasonal variation of polysaccharides in surface sediments.

No specific seasonal trend was observed for SMCHO. But for STCHO and SPCHO, the trend was postmonsoon > monsoon > premonsoon. ANOVA result also confirmed this, which showed that both STCHO and SPCHO showed significant seasonal variation (Table B.7). Carbohydrates showed a general distribution pattern marked by higher values synchronizing with excessive run-off during postmonsoon and monsoon and also due to clayey nature of the sediment during this period.

The abundance of carbohydrates in the sediments of Cochin mangroves may thus reflect the contribution of autochthonous mangrove sources. Results of ANOVA revealed a significant difference between stations for all the types of carbohydrates (Table B.7). The low carbohydrate content at Station 3 might be due to sandy texture of the sediment and also due to high tidal activity. High values at Station 2 might be due to low tidal flushing and clayey nature of the sediment. The interaction of organic matter (OM) with solid surfaces is an important process in the biogeochemical cycling of carbon in aquatic systems (Ding and Henrichs, 2002). Adsorption of OM to sediment particles can decrease its availability to microbial degradation (Sugai and Henrichs, 1992; Mayer, 1994a,b; Hedges and Keil, 1995). Therefore, adsorption and desorption behavior of organic substances may partially explain the selective decomposition and long-term preservation of organic carbon in mangrove environments (Henrichs and Sugai, 1993). Adsorption to particles also is apparently a key process in the transport and deposition of OM (Hedges and Keil, 1995; Henrichs, 1995). Gong and Ong (1990) observed that highest decomposition rates occurred in sites with the most frequent tidal inundation where leaves were submerged most of the time, and that in the less inundated areas, leaves decomposed more rapidly during high rainfall periods. He

also observed that the macro-invertebrates (mainly sesarmid crabs) played an important role in decomposition wherever their density was high (Gong and Ong, 1990). Corrlation data (Table C.10a-c) showed that at Station 1, all the three forms of carbohydrates showed positive relationship with organic carbon suggesting that carbohydrates be enriched in organic carbon. Here monosaccharides showed positive correlation with free amino acids. This suggests that monosaccharides and free amino acids have same rate of formation and degradation. Monosaccharides and polysaccharides showed positive correlation among themselves at Station 2 and Station 3 suggesting that increase in polysaccharide concentration increases the monosaccharide content by the hydrolysis of the former. Polysaccharides showed positive correlation with total lipids and organic carbon at Station 2 suggesting that polysaccharides and lipids have similar rate of formation and degradation and/or due to their same source i.e., their source and fate may be influenced by same environmental processes.

Mean values of STCHO-C% of SOC after normalizing with carbon for each station were 10.78%, 7.51% and 10.23% at Stations 1, 2 and 3 respectively (Table A.48). Contributions of carbohydrates to the total organic carbon pool were maximum at Station 3 and least at Vypin mangroves, i.e., Station 1 and Station 2. ANOVA showed no significant difference between stations and seasons (Table B.9a). But the high mean value obtained at Station 3 might be due to presence of fresh organic matter, being removed by intense tidal activity. The low value at Vypin mangroves (Station 1 and Station 2) may be due to the isolated conditions with no tidal flushing forcing them to remain in the system for consumption by benthos. Raghukumar et al. (1995) observed rapid loss of detrital dry weight and a reduction in proteins, carbohydrates, reducing sugars, phenolics and cellulose by the sequence of colonisation, densities and biomass of fungi, thraustochytrid protists and bacteria during decomposition of leaves of the mangrove Rhizophora apiculata. The organic matter remaining may contain only the refractory compounds. The active hydrodynamical (resuspension) and biological (consumption, bioturbation) events participate in the frequent reworking of the superficial deposits (muddy-silts) and, consequently, the active degradation (oxidization) of the organic matter (Buscail et al., 1995). Similar results were obtained for Lacerda et al. (1995) who reported variation of STCHO-C(%of SOC)

in the core sediments of Avicennia soil in South-eastern Brazil from 0.23mg/g to 4.28mg/g and that of Rhizophora soil almost constant values were obtained.

- *Sedimentary Total Lipids (STL)*

Lipids, defined as compounds soluble in organic solvents and only slightly soluble in water, include many well-studied groups of chemicals including hydrocarbons, sterols, fatty acids and fatty alcohols. Organic functional groups are altered during biogeochemical reactions in the water column and sediments, and it is possible to use changes in molecular structure to follow reaction mechanisms. Ratios of stanol to stenol have been used as indicators of redox conditions in the water columns progressing from oxic to suboxic and anoxic and downcore in reducing sediments; sterenes are abundant in suboxic seawater (Wakeham et al., 1984). As organic matter is further altered during maturation of ancient sediments, steroidal compounds that have survived burial in recent sediments are transformed to the saturated and aromatized steroidal hydrocarbons (steranes) that are widely used biomarkers in petroleum geochemistry.

In the present study, Station 3 exhibited low lipid content throughout the study period and the lowest of all observed was 0.586mg/g in April'00. There was a very distinct peak (10.995mg/g) in September'00 at Station 2 (Table A.45). The annual mean values for each station were 3.52mg/g, 3.91mg/g and 1.295mg/g at Stations 1, 2 and 3 respectively with an overall mean value of 2.80mg/g..

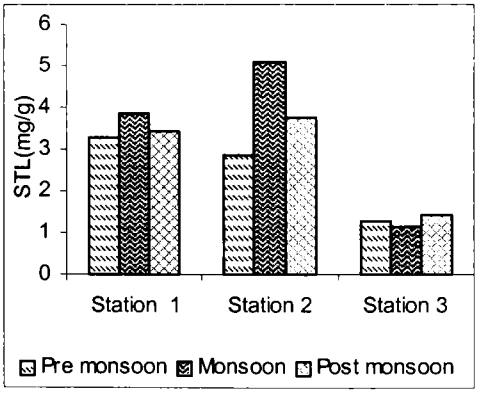


Figure 6.11: Spatial and seasonal variation of total lipids in surface sediments.

Seasonal mean values recorded the highest at Station 2 during monsoon and the lowest at Station 3 during monsoon Thus, when Stations 1 and 2 showed the

peak during monsoon, Station 3 showed a minimum during this season (Fig. 6.11). Lipid content was very low at Station 3. High lipid content at Station 2 might be due to high organic matter and clay content which preserves lipids by adsorption onto the surface thereby preventing microbial and oxidative degradation. It must be realized that the changes in the amount of various grain size fractions can significantly influence the chemical compositions of the sediments (Romankevich, 1984). The organic matter in the sediments increased as the particle size decreased. Transk(1968) established that silts contained twice as much and clayey silts 4 times as much organic matter as sands. The sediment texture thus plays a vital role in the retention of organic matter. The flooding and ebbing of tidal waters promote wash off of finer particles, particularly silts and clays, along with organic matter leaving the coarser sand grains as lag concentrates. Decomposition rates may vary significantly among mangrove plant species, with differences related to anatomy and chemical composition (Benner et al., 1990a). Furthermore, the fragmentation and consumption of mangrove leaves by crabs may increase the decay rates by upto 2 orders of magnitude (Kristensen and Pilgaard, 1999). Correlation data (Table C.10a-c) exhibited that at Station 1 and Station 2 total lipids showed positive correlation with polysaccharides and at Station 2 and Station 3 lipids showed positive correlation with organic carbon. This means that at Station 1 and Station 2, formation and degradation of lipids takes place at the same rate as that of polysaccharides and at Station 2 and Station 3, lipids are enriched are preserved in organic matter.

Mean values of STL-C% of SOC were 4.56%, 3.81% and 3.69% at Stations 1, 2 and 3 respectively (Table A.50). The low lipid contribution of Station 3 to organic carbon pool may be due to high rate of degradation in oxic environment. The sandy nature of the sediment allows the intrusion of oxygen evenly to the sediments thereby projecting lipids to microbial or chemical degradation. Also dissolved oxygen content of Station 3 waters was quite high. The major effect of selective degradation/preservation is that the lipid composition of sediments may be highly altered compared to the source materials. Relatively less is known about rates of lipid degradation. de Baar et al.(1983) found that the rate of net loss of fatty acids increased with number of double bonds and decreased with the number of carbon atoms. Using laboratory simulations, Harvey and co-workers (Harvey et

al., 1995; Harvey and Macko, 1997) have compared the kinetics of phytoplankton decay under oxic and anoxic conditions: in addition to lipids, their study examined organic carbon, nitrogen, carbohydrates and aminoacids. Among the major biochemical fractions, carbohydrates were most rapidly degraded under oxic conditions, followed by protein and lipid. Degradation rates for all components were significantly lower under anoxic conditions. Similar comparisons of degradation of various organic matter pools in oxic and anoxic regimes have been made in the water column and sediments (Lee, 1992). However, a recent analysis of sedimentary lipid degradation in a variety a sediments having widely different accumulation rates indicates that degradation rates in fact vary as a function of time since burial. The highest rates and rate constants occur in surface sediments, and the time scale used in calculating degradation rates thus becomes crucial.

➢ ***Spatial and Temporal Variation of Sedimentary Refractory Constituents***

- *Sedimentary Tannin and Lignin (ST&L)*

Phenolic compounds (T&L) are one of the major groups of secondary metabolites in plants. Other sources in sediment are flavanoids leached from plant debris and those synthesized by soil micro organisms. Lignin is a main component of wood and occurs in the cell walls of all vascular plant tissue. Leaves and other herbaceous plant tissues, however, often contain varying amounts of other components, such as cyclitols, tannins, and the aliphatic constituents of cuticles, that can account for a substantial fraction of the total organic matter (Kolattukudy and Espelie, 1985). Waters in the vicinity of decaying leaves are often "tea-colored" due to the relatively high concentrations of DOM that contain tannins and other phenolic compounds (Benner et al., 1990a).

It is probably because of its heteropolymeric structure of phenyl-propanoid that lignin is hardly accessible to most microorganisms, building a relative stable biopolymer. These features make lignin a unique tracer for vascular plant matter, suitable even for the chemotaxonomic distinction between angiosperms, gymnosperms, and non-woody vascular plants (Hedges and Mann, 1979). In nature, phenol will form complexes with nitrogenous compound like proteins and free amino acids and makes them less susceptible for microbial degradation. This reduces mineralization and release of nutrients (Joseph and Chandrika, 2000).

Therefore, the abundance of phenolics in sediments plays an important role in nutrient cycling.

The present study reports on the abundance and seasonal variation of phenolics in the mangrove sediments of Cochin along with other environmental parameters (Table A.46 and Fig. 6.12). Throughout the study period, Station 3 showed the lowest T&L concentrations when compared to the other two stations, the lowest (1.22mg/g) was found at Station 3 in December'99. The maximum (6.84mg/g) was found to be in February'00 at Station 1. The mean value of tannin and lignin content at Station 1, 2 and 3 were 4.36mg/g, 4.03mg/g, 1.71mg/g, overall mean value being 2.68mg/g. Station 3 showed comparatively low value. Seasonal variation showed highest of T&L at Station 1 during premonsoon and lowest at Station 3 during premonsoon.

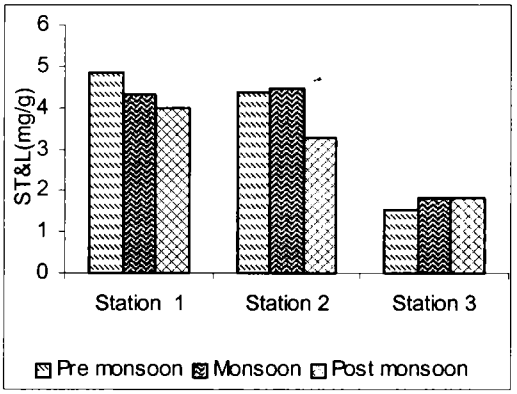


Figure 6.12: Spatial and seasonal variation of tannin and lignin in surface sediments.

The differences in mangrove sediment chemistry of tannin and lignin could be due to either species-specific processes or to differences in elevation at which these mangrove types occur. Differences in elevation relate directly to differences in tidal inundation frequencies, litter input and aerial exposure. An accumulation of lignin in sedimentary organic matter of Station 2 might be because of the fact that lignin degradation is considered to be slow under anaerobic (anoxic) conditions (Dittmar and Lara, 2001). At Station 2 isolated condition prevents any washing out of organic matter from the system and hence remain in the system itself, accumulating in the sediment. At Station 3 tidal flushing removes the organic matter from the surface sediment and sandy nature allows the degradation to takes to takes place more

rapidly allowing the microbes and oxygen to infiltrate into the sediment. Also the low turbidity at this site allows the sunlight to pass through the water column to reach the surface sediment, allowing photodegradation to occur. Lignin, has been suggested to be selectively degraded by photochemical reactions (Ertel,1990). Tannin and lignin showed positive correlation with humic substances at Station 2, which is attributed to the fact that both are refractory to microbial degradation. High concentrations of tannins may hamper colonization by the macrobenthos (Lee, 1999). Alongi (1987) observed that mangrove-derived tannins negatively effected laboratory-reared nematode populations and natural communities of meiobenthos in tropical mangrove forests along the northeastern coast of Australia. Two-way ANOVA for tannin and lignin showed significant difference between stations but no significant variation between seasons (Table B.7).

At Station 3, T&L showed an inverse correlation with pH ($r = -0.966$, $p<0.1$). An acid-generating mechanism in mangrove sediments may be leaching of polyphenolic acids from the standing amounts of leaf litter and slash lying on, and buried in, these sediments (Kristensen et al., 1991). Polyphenolic acids are a major component of pore-water DOC pools (Boto et al., 1989) and DOC leaching from mangrove leaves (Alongi et al., 1998). The activities of Rhizophora apiculata roots are known to lower the pH and alkalinity of sediments (Kristensen et al., 1991). Mangrove trees grow under reductive and sometimes acidic conditions, both of which are injurious to the root growth. The large amount of tannins combines with ferric ion in the soil solution resulting in the blackening of the roots due to the formation of a tannin-ferric iron complex (Kimura and Wada, 1989). It was considered that the tannins in mangrove tree roots combine with iron in the soil solution, to alleviate the iron excess damage. The tannin-ferric iron complex thus formed counteracts the hydrogen sulfide toxicity to roots by oxidation. At Station 1 and 2, positive correlation of tannin and lignin with Iron [($r = 0.838$, and 0.892 respectively), $p<0.1$] showed the possibility of tannin-ferric iron complex formation. No such correlation was obtained at Station 3, may be because of sandy nature of the sediment.

During the three seasons, T&L showed significant positive correlations with almost all organic constituents and also with clay and silt and a negative correlation with sand percentage (Table C.11a-c). Significant positive correlation with

polysaccharides suggests their same source and rate of reactions. In vascular plants, polysaccharides are typically found to be more reactive than lignins, resulting in the gradual enrichment of the remaining detritus in lignin-derived carbon (Benner et al., 1987; Spiker and Hatcher, 1987). Contrary to what has been observed in a variety of other vascular plant tissues, the lignin component of mangrove leaves was lost at approximately the same rate as the polysaccharide components (Benner et al., 1990a). This observation suggests that the same molecules may exhibit variable relative reactivities in different plant tissues, so that it will be necessary to define the chemical "architecture", as well as the composition, of individual types of vascular plant tissues before their decomposition can be understood and predicted. Leaching was the major initial pathway for the loss of lignin from decaying mangrove leaves (Benner et al., 1990a). Lignin that is leached from plant material can have compositional characteristics that are distinct from the lignin polymer remaining in the plant tissue. Fungal degradation which is thought to be the principle mechanism for the biological cycling of lignin, causes oxidation of the propyl side chains, demethylation of the 3-and 5-methoxyl groups, and aromatic ring cleavage (Filley et al., 2000).

- *Sedimentary Humic substances (SHS)*

Humic and fulvic acids are believed to be formed in the sediments through diagenetic transformation of organic matter, the by-product being resistant to biochemical degradation (Sardessai, 1989). The characteristics of humic substances differ significantly in varied depositional environments. The diagenetic transformation of organic matter into humic substances and the magnitude of humification depend upon the nature of the organic matter and several other environmental factors (Rashid, 1985) such as the redox character, sediment texture, hydrodynamic conditions, topographic characteristics of the region etc. The proportion of humic substances to the organic matter of sediments also depends upon a number of geological, geochemical and depositional conditions [Rashid, 1985]. But the abundance of these acids in the sedimentary organic matter depends largely on the nature and amount of the substrate, the microbial population and the hydrographic and bathymetric conditions of the ecosystem. However, the other environmental factors like primary productivity, sediment texture and microbial

activity also play a significant role in the humification process [Joctour Monrozeir et al.. 1983].

The components of organic matter from which humic substances are formed range from carbohydrates, proteins to lignins. The properties of the starting material from which these substances are formed are reflected in their structures. Amino acids derived from proteinaceous as well as non-proteinaceous sources participate in various geochemical processes that lead to the formation of humic molecules and are probably one of the major aliphatic structural units of the peripheral portion of these compounds (Maita et al., 1982). Amino acids constitute apparently about 7.5 to 10% of humic substances in recent marine sediments and soils (Rashid, 1972), whereas Felbeck (1971) stated that 20 to 50% of the nitrogen in most humic compounds is amino acids. Amino acids make up approximately 10% by the weight of the humic components extracted from soil. Thus, amino acids are one of the major building blocks of humic compounds (Sardessai, 1999). Humification of the organic matter depends on the physico-chemical and biological conditions of the environment which may promote or retard mineralisation, assimilation and polymerization reactions (Gadel, 1980). These effects control the subsequent distribution and evolution of humic compounds. Thus the hydrodynamic conditions, the redox character, the sedimentation rate and temperature control humus formation and in many instances, transform their physico-chemical properties.

Humic substances play a significant role in the biological cycle in aquatic environment. Its importance in complexing the toxic heavy metals and in recycling the essential trace metals required for the growth of phytoplankton has been well realized. However, the information on the humic acid fraction of the organic matter in sediments is scarce in mangrove ecosystem especially in Cochin mangroves. Shanmukhappa and Neelakantan (1989) found average SHA concentration of 2.54mg/g in mangrove habitats of Karwar, west coast of India.

Seasonal variations of these materials in surface and core sediments of mangrove ecosystems have not been studied earlier. The present study reports on monthly (Table A.47) and seasonal variations (Fig. 6.13) of humic substances in this organically rich and productive environment with a minor comparison with the adjoining estuarine system of Cochin.

A distinct peak (32.12mg/g) for SHS was observed at Station 2 in April'00 in the present study. A second largest peak was observed at Station 1 in March. The lowest concentration (0.458mg/g) was found at Station 2 in April'99. The mean values of each station were 15.09mg/g, 18.04mg/g and 9.1mg/g for Stations 1, 2 and 3 respectively with an overall mean value of 13.25mg/g. The seasonal fluctuation showed a minimum at Station 2 during monsoon and a maximum at Station 3 during pre-monsoon. Station 1 and Station 2 showed similar trend with premonsoon exhibiting high humic substances and postmonsoon with low. At Station 3, the seasonal maximum and minimum were during post-monsoon and pre-monsoon respectively.

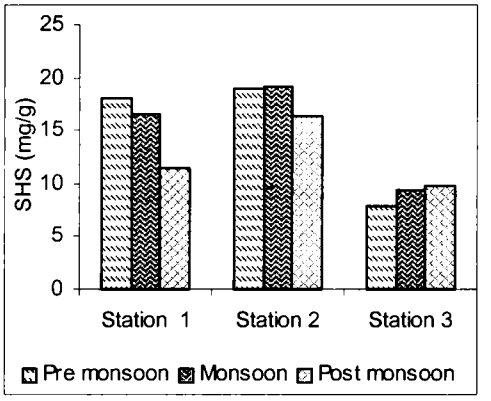


Figure 6.13: Spatial and seasonal variation of humic substances in surface sediments.

ANOVA showed that there is significant difference between stations (Table B.7). A comparison of the concentrations of humic substances at the three stations depicts that in general, Station 2 has a high concentration of humic acids as compared to Station 1 and Station 3. Station 2 is characterized by a thick population of mangroves. Besides, the area is cut off from the estuary during the low tides which also helps in the retention of organic matter. Station 3 receives a part of its supply of organic matter from the fresh water, which is so evident from the low salinity at this station relative to Station 1. Station 1 is dominated by salt water for a greater part of the year and although the water column is influenced by mangrove community, the area has free access to the estuary even during low tide. The high content of humic acid at Station 2 might be due to adsorption onto clay minerals and high organic matter load. The humic substances accounted for 66 to

82% of organic matter in the surface sediments and deeper sections in the organic rich sediments of the Peru continental shelf (Poutanen and Morris, 1983). Some of the factors influencing the humification process are oxygen content and the clay minerals (Sardessai, 1999). Carbohydrates and amino acids are probably the most predominant components of organic matter. A vast group of microorganisms attack proteins and organic compounds to produce amino acids and it is generally recognised that most carbohydrates and amino acids in water column and aquatic sediments exist in some sort of association, forming macromolecular material that is resistant to degradation (Handa, 1970). Further transformation of this material results in the production of humic compounds (Sardessai, 1999). High carbohydrates and amino acids observed in this station provides a clue to this type of humic substance formation. Also as, explained for the previous compounds, isolated condition with low tidal flushing and increased organic matter input increases the humification process. Leenheer (1980) reported the enrichment of humic acids on detritus and in sediments of the Rio Negro and suggested that this is due to adsorption of the more hydrophobic humic acids onto the sparingly available particle surfaces. But at Station 3 high tidal inundation cleanses away the organic matter as soon as it is formed without giving a chance for humification to occur. The sandy nature of the sediment and its low organic matter content avoid any sort of adsorption, allowing easy attack of fresh organic matter as well as humic substances, if any formed, either chemically or microbially. At Station 1, SOC was enriched with humic substance as shown by their positive correlation (Table C.10a-c), but at Station 3 organic carbon was depleted in humic substances. At Station 1 and Station 2, humic substance showed a negative effect on combined amino acids and linear relationship with tannin and lignin at Station 2.

It can be observed that the concentration of humic substance was generally higher during premonsoon and lower during monsoon season except at Station 3, which showed the lowest concentration during premonsoon. The processes like litter fall, degradation, resuspension and the variability in the transport of organic matter to the mangrove ecosystem during different seasons play a significant role in the humic substance concentration in the mangrove ecosystem (Sardessai., 1993). High values during premonsoon at Station 1 and Station 2 might be due to adsorption onto clay minerals and organic matter, which were also maximum

during this period. Twilley et al. (1986) found that average litter production to be the highest in the premonsoon and the lowest during monsoon for the four major mangrove species at Chorao island. Lu and Lin (1990) also observed a peak fall in summer season and very low fall in winter. High temperature, longer durations of light, higher evapotranspiration rate during summer months are probably the factors responsible for the greatest litterfall at this time (Chale, 1996 and Tam et al., 1998). Litter production has been widely used as a measure of productivity, especially in view of its contribution to the estuarine systems (Bunt, 1995; Chale, 1996 and Kadlec and Knight, 1996). The decomposition rates of mangrove litter depend on the degree and frequency of tidal inundation, climatic and edaphic factors, and the presence or absence of litter- consuming fauna within forests (Chale, 1993). Thus, the dynamics of litter breakdown will also vary geographically. In addition, litter decomposition rates vary significantly between plant species, affected by leaf anatomy and chemical composition in particular, the internal nutrient and lignin concentrations (Tam et al., 1998). The mangrove litter undergoes degradation by bacteria and fungi. It can be concluded that the litter fall mainly contributes to the high concentration of organic matter and humic acids observed in the premonsoon. The humic acids in the sediments of these mangrove ecosystems are contributed mainly by the decomposition of the litter and partly by the fresh water influx during the monsoons (Sardessai, 1993). Low values at Station 3 during the same season might be due to maximum intensity of sunlight, which initiates photodegradation during this period. Photodegradation can change the presumably refractory organic matter to low-molecular-weight, biologically labile compounds (Kieber et al.,1989) or volatile inorganic compounds (Valentine and Zepp,1993; Allard et al.,1994; Miller and Zepp,1995). Lignin has been suggested to be selectively degraded by photochemical reactions (Ertel, 1990). These findings suggest that humic substances might be cycled faster and along other pathways than earlier believed, and indicate that photochemical degradation might play a significant role (Skoog et al., 1996).

Humification process in the present study was not a function of organic carbon content during monsoon and premonsoon, showing only a positive relationship during postmonsoon only. The texture of the sediment showed a highly

significant relationship with humic substances (positive with clay percentage and negative with sand content) during all the seasons (Table C.11a-c).

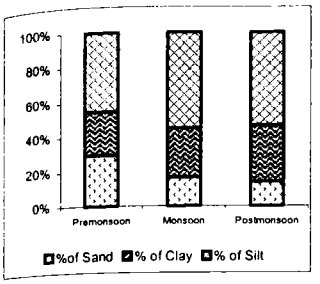


Figure 6.14a: Percentage fraction of sand, clay and silt in surface sediments at Station 1

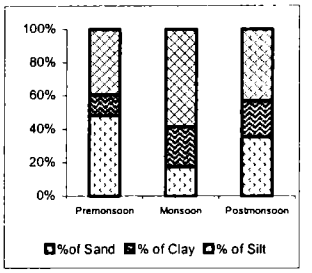


Figure 6.14b: Percentage fraction of sand, clay and silt in surface sediments at Station 2

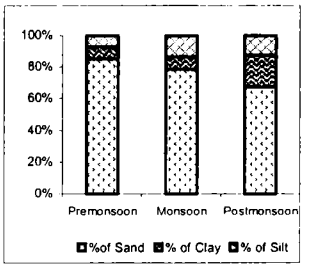


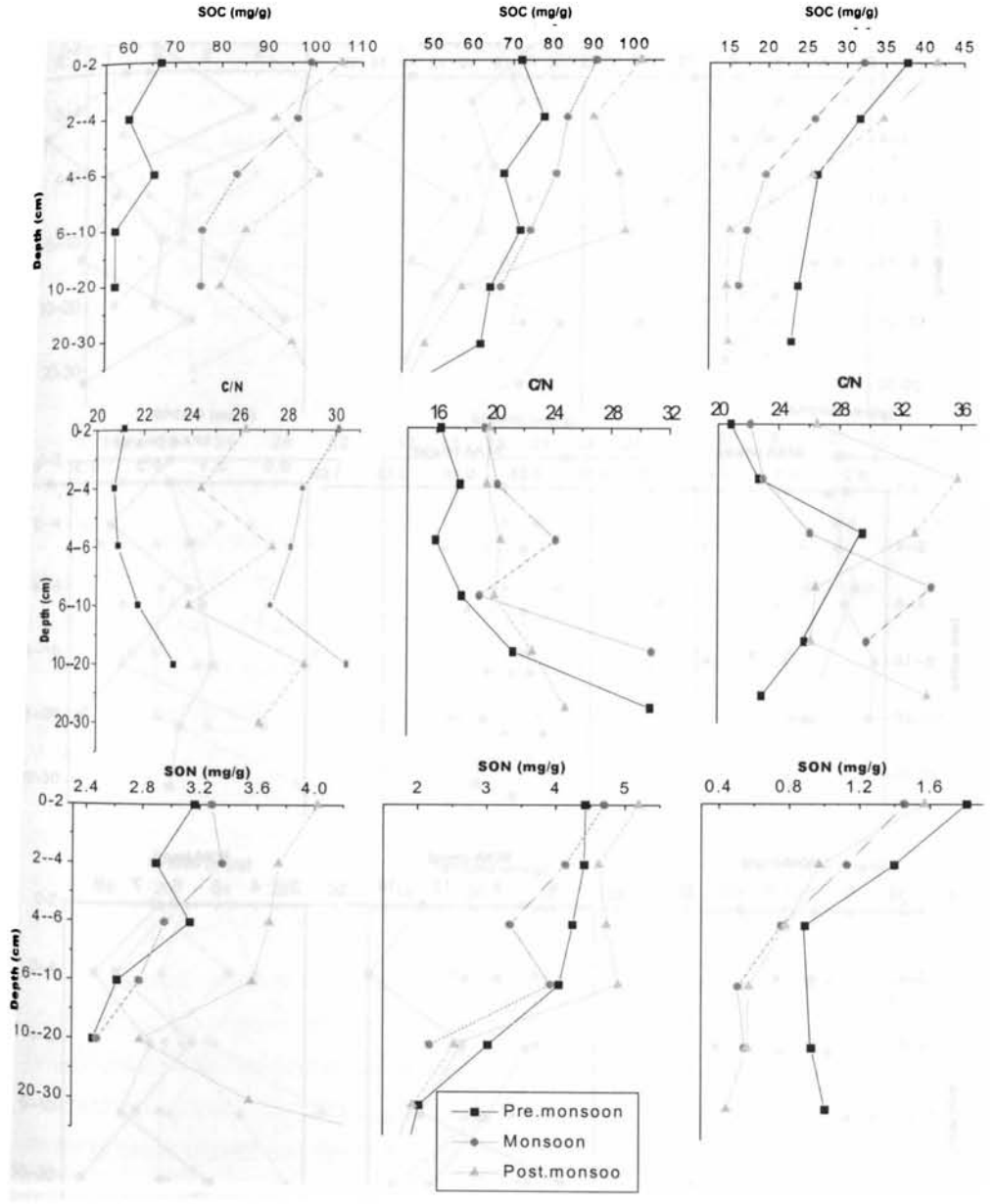
Figure 6.14c: Percentage fraction of sand, clay and silt in surface sediments at Station 3

5.2.2 Core sediments

Three way-ANOVA showed a significant difference between stations and seasons for all the parameters studied except for SFAA (Table B.8a,b). Least significant difference (LSD) analysis showed difference between Vypin stations (Station 1 and Station 2) and Aroor station (Station 3). Thus Stations 1 and 2 behaved similarly for most of the parameters. Figures 6.15 to 6.18 depicts the down core variation of various organic constituents in core sediments at Station 1 to 3. In these stations sediment texture showed high clay and silt content Figures 6.19a-c. Clay + silt constitute 62.32 – 95.2% at Station 1 and 38.95 – 87.44% at Station 2. But at Station 3, sand was the major fraction (74.56 – 85.36%). Factors that contribute to the higher organic matter content may be the fine nature of sediments (clayey and silty sediments) and high rate of sedimentation. Clayey silt sediments dominate first two study areas. The negative correlation of organic matter with sand and positive correlation with the clay and silt can be related to the terrigenous nature of the organic matter. The lower organic matter content in the deepest layers may be due to coarse nature of sediments and this change in organic matter values is very high (Reghunath and Sreedhara Murthy, 1996). The organic carbon distribution in mangrove sediments is controlled mainly by the textural attributes of sediments. In the present study, the lowest organic carbon content in the surface and core samples are observed in the sand-dominated sediments in the three mangrove areas studied. Increase in organic carbon with decreasing grain size is

axiomatic. Coarse sediments aid destruction of organic matter by permitting easy diffusion of free oxygen and oxidising salts resulting in lower organic carbon contents. Whereas, clay-rich sediments protects organic matter from oxidation leading to their better preservation (Paropkari et al., 1992). According to many investigators, the association of organic carbon in finer sediments might be due to the enhanced surface area of the finer particles, which in turn promotes the absorptive ability of organic colloids and also traps finer organic particles intact (Seralathan and Padmalal, 1993). The low carbon content of Station 3 might be due to the wash-off of organic particles/materials by tides/waves. The less dense mangrove vegetation of this region is another factor promoting selective erosion of finer particles from the sedimented population. At the same time, the Station 1 and Station 2 are often protected from the leaching of organic carbon by the thick mangrove canopy with its tightly knitted root systems. Contrast to the Station 3, Station 1 and 2 are affected by low energy tidal currents and luxuriant mangrove cover. The flood and ebb of tidal waters constantly winnows the finer particles like silt and clays to the neighboring ecosystems, leaving the more coarser grains rich in sand in situ. While the low energy tidal currents is insufficient in the effective winnowing of finer particles, the luxuriant mangrove forests and its root systems effectively traps the finer particles and thereby stabilizing the mangrove forested area from erosion threats. The substantially high content of mud over sand in this area exemplifies the ability of mangrove vegetation in trapping finer particles in the sediment substratum. Mangrove sediments of Station 1 and Station 2 are generally well-sorted silts and clays (Fig.6.19a-c) with variable quantities of fine, fibrous root matter and spongy wood material. In core sediments, the top most part exhibited a higher concentration of organic carbon and does not exhibit uniformity in its variation further downward (Sunil Kumar, 1996). The waxing and waning of organic carbon in the sediment core could be attributed to the compaction, degradation and decomposition during diagenesis.

Fig.6.15 Spatial, seasonal and downcore variation of organic carbon, C/N and organic nitrogen in core sediments



Station 1 Station 2 Station 3

Fig. 6.16 Spatial, seasonal and downcore variation of total, free and combin ed amino acids in core sediments

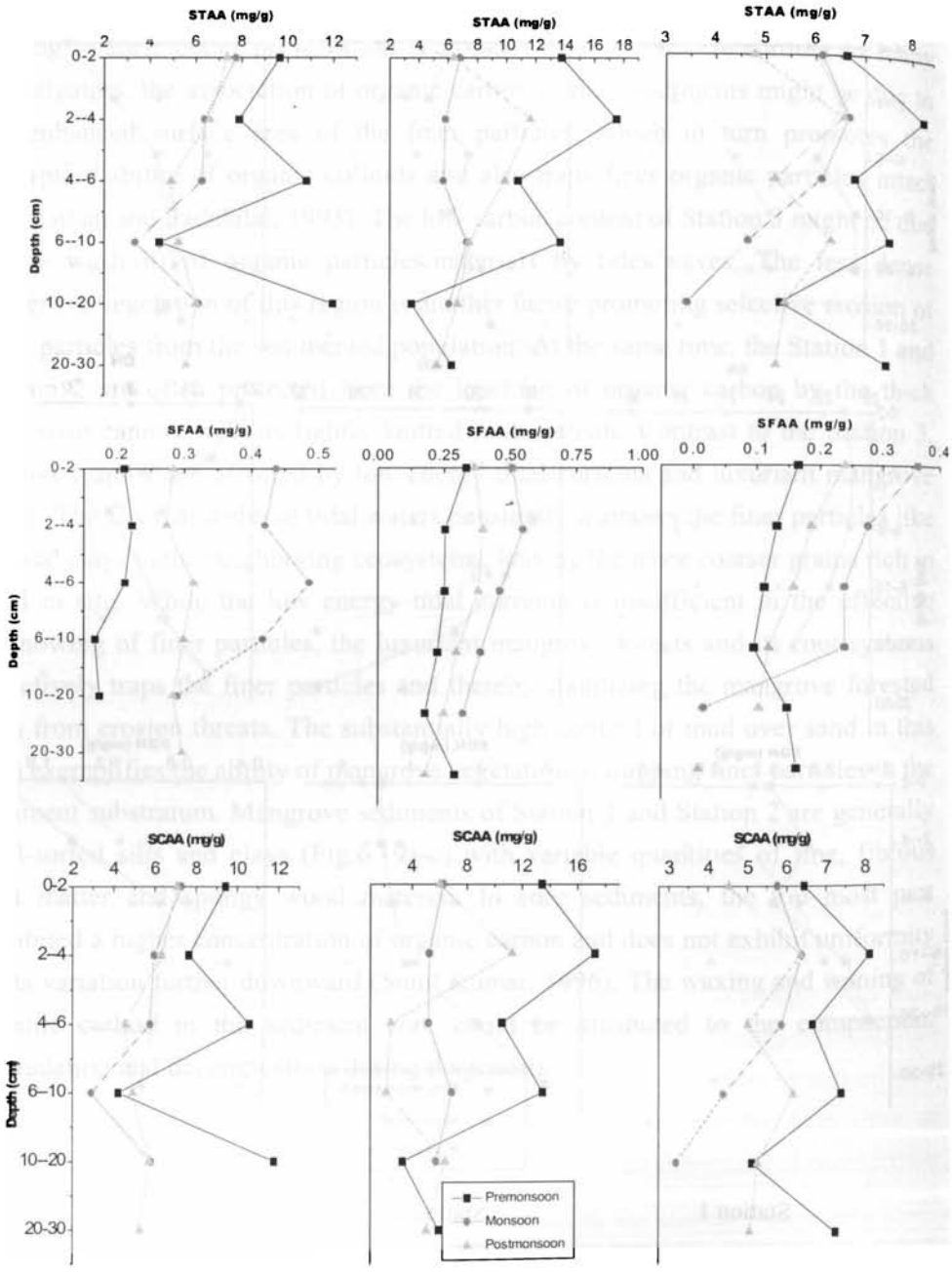
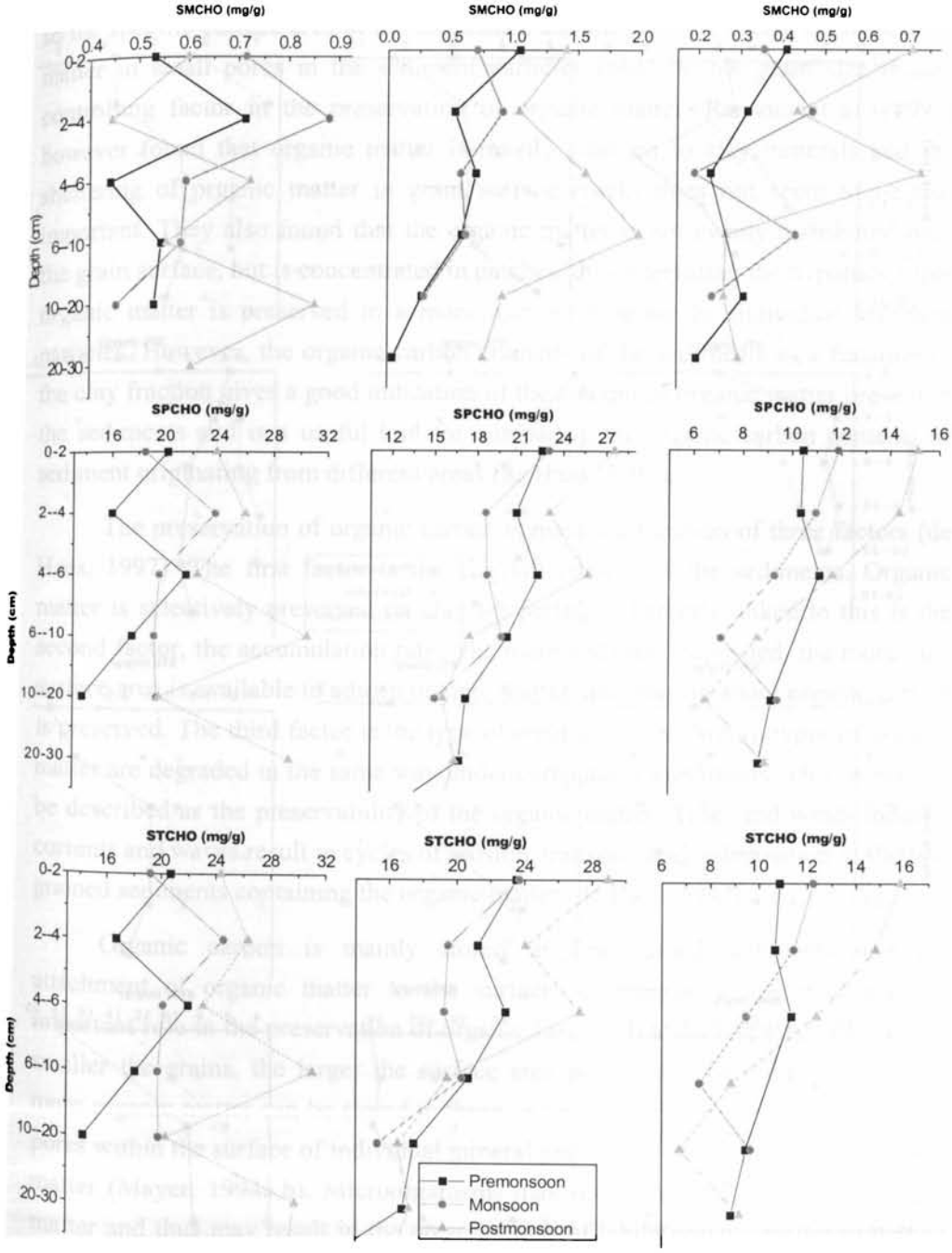
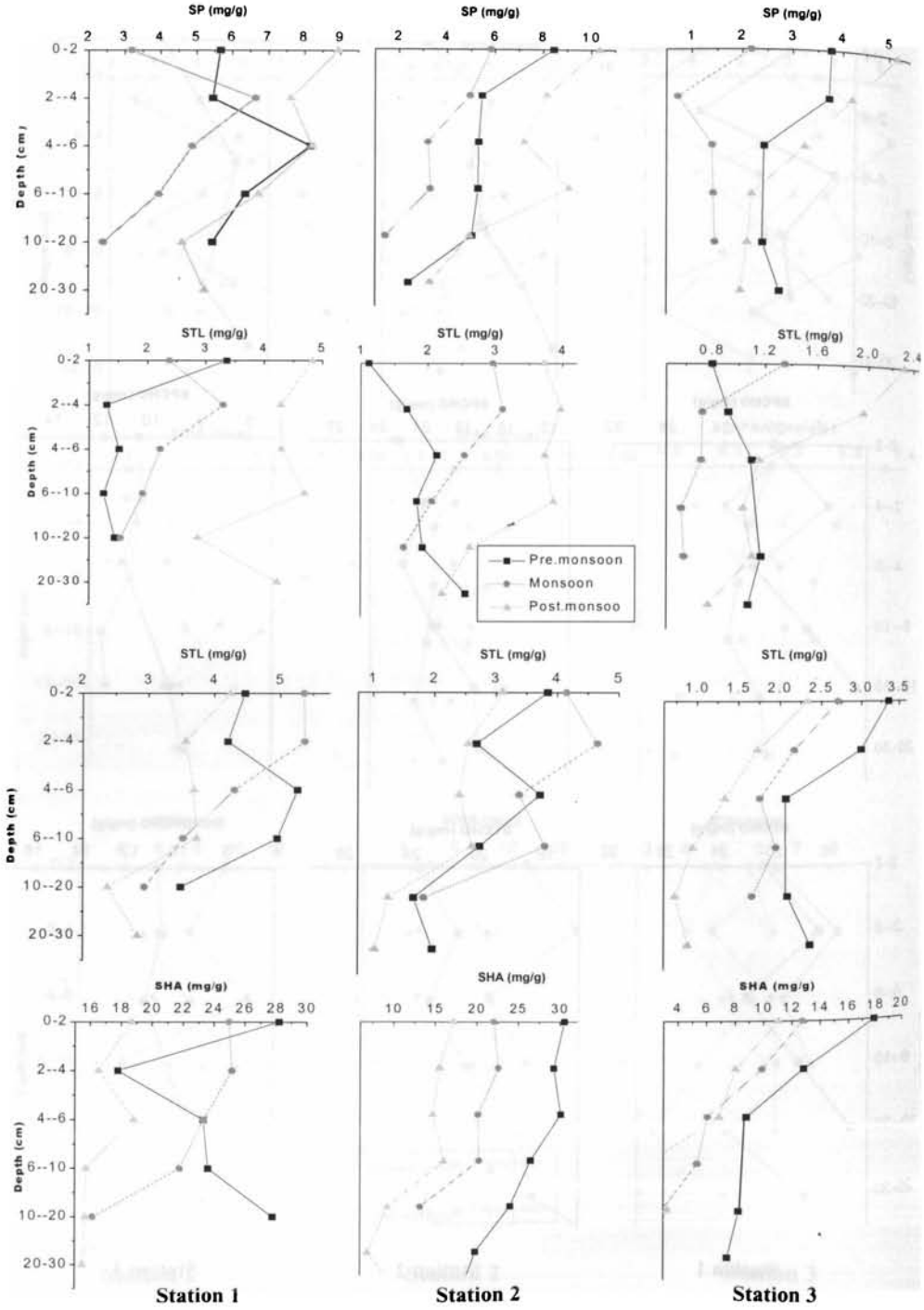


Fig. 6.17 Spatial, seasonal and downcore variation of carbohydrates in core sediments



Station 1 **Station 2** **Station 3**

Fig. 6.18 Spatial, seasonal and downcore variation of proteins, lipids, tannin and lignin and humic substances in core sediments



From Keil et al. (1994) and Mayer (1994a,b), it follows that not the grain size itself, but the sorption of organic matter to the surface of the individual grains, so the specific surface area of the sediments, and the possible sheltering of organic matter in small pores in the sediment particles could be the grain size related controlling factor in the preservation of organic matter. Ransom et al. (1997) however found that organic matter is mainly attached to clay minerals and the sheltering of organic matter in grain surface cracks does not seem to be that important. They also found that the organic matter is not evenly distributed over the grain surface, but is concentrated in patches, thus enervating the hypothesis that organic matter is preserved in a monolayer enveloping the individual sediment particles. However, the organic carbon contents of the sediments as a function of the clay fraction gives a good indication of the amount of organic matter present in the sediments and is a useful tool for comparing the organic carbon contents of sediment originating from different areas (de Haas, 1997).

The preservation of organic carbon is mainly a function of three factors (de Haas, 1997). The first factor is the clay/silt content of the sediments. Organic matter is selectively preserved on clay/silt particles. Directly linked to this is the second factor, the accumulation rate. The more sediment deposited, the more clay surface area is available to adsorb organic matter, and thus the more organic carbon is preserved. The third factor is the type of organic matter. Not all types of organic matter are degraded in the same way under comparable conditions. This factor can be described as the preservability of the organic matter. Tide- and wind- induced currents and waves result in cycles of erosion, transport and redeposition of the fine grained sediments containing the organic matter (de Haas, 1997).

Organic carbon is mainly stored in fine-grained sediments and the attachment of organic matter to the surface of material grains may play an important role in the preservation of organic carbon (Hedges and Keil, 1995). The smaller the grains, the larger the surface area per volume of sediments and the more organic matter can be stored in these sediments (de Haas et al., 1997). Small pores within the surface of individual mineral grains may act as shelters for organic matter (Mayer, 1994a,b). Microorganisms may not be able to reach this organic matter and thus may result in the preservations of labile organic matter in marine sediments (Keil et al, 1994). However, Pedersen (1995), Berner (1995), Mayer

(1995), and Hedges and Keil (1995) argue that not only adsorption of organic matter to the surface of mineral grains, but also other factors (setting flux, availability of oxygen) play a role in the preservation of organic carbon.

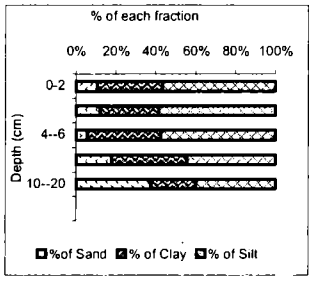


Figure 6.19a: Spatial, seasonal and downcore variation of Percentage fraction of sand, clay and silt at Station 1

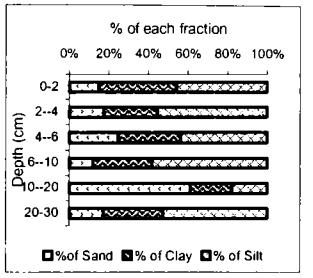


Figure 6.19b: Spatial, seasonal and downcore variation of Percentage fraction of sand, clay and silt at Station 2

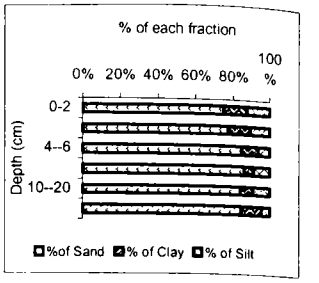


Figure 6.19c: Spatial, seasonal and downcore variation of Percentage fraction of sand, clay and silt at Station 3

Although, all the organic compounds under study showed significant difference between seasons, no specific trends could be identified in their fluctuations.

Spatial, seasonal and downcore variation of all organic constituents are depicted in the figures (Fig. 6.15 to 6.18). The total organic carbon content and all its constituents varied spatially, seasonally and downcore. The minimum SOC content was 14.69mg/g at 10-20cm depth at Station 3, the maximum was 105.5mg/g at 0-2cm at Station 1. In general, the cores showed a downcore decrease in organic carbon concentration. In some cores the organic carbon concentration decreased to a stable value, in others it did not. The decrease in the organic carbon contents could be very smooth, or irregular. The downcore organic carbon contents locally may show a small sudden increase as well, which might be due to the presence of root matter. The slight downcore decrease of organic carbon in some cores is thought to result from the extensive bioturbation in those cores. Downcore variation shown by almost all variables could be due to several factors. A continuum of bioturbation and cycles of erosion, transport and redeposition takes place under the influence of tidal currents. These processes result in succesive periods during which the organic matter is under the influence of oxic and anoxic conditions, which affects the degradation of the organic matter (Hedges et al.,1999). The reason for Station 1 and Station 2 being the most important sink for

organic carbon and its constituents is the huge amount of fine grained sediments being deposited here. Other factors that play a role in the preservation of organic matter and that are related to sediment grain surface conditions are the sheltering of organic matter by small pores in sediment particles (Mayer, 1994a,b) and the possible sorption of organic matter to mineral surfaces of fine grained sediments. This causes a part of the labile components of organic matter to be unavailable for oxidation by micro-organisms and to be buried in the sediments (Keil et al., 1994). The observed relationship between texture and organic matter contents (Table C.12a, b) suggests that changes in grain size with time may result in changes in the burial rate of organic carbon. Spatial variations in grain size result in spatial variations in organic matter burial. Almost all organic constituents showed significant positive correlations with organic carbon, organic nitrogen, silt and clay and negative correlation with sand in almost all depths (Table C.12a, b). Also, for all parameters, each depth showed significant intercorrelations with every other depths (Table C.13a,b). This may be due to translocation of oxygen by roots, pore water, bioturbating crabs, benthic infauna etc.

As the oxic zone in coastal sediments usually is limited to a thin uppermost layer, a large fraction of the organic matter is buried in a more or less decomposed form into anoxic layers. Mutualistic consortia of bacteria accomplish anaerobic decomposition because no single type of anaerobic bacterium seems capable of complete mineralization (Fenchel et al., 1998). The large and normally complex polymeric organic molecules are first split into smaller and water soluble moieties (organic acids like formate, acetate, propionate etc.) and inorganic nutrients by hydrolysis and fermentation (Kristensen and Hansen, 1995; Holmer, 1999). The small organic acids are then oxidized completely to H_2O and CO_2 by a number of respiring microorganisms using a variety of inorganic compounds as electron acceptors (e.g., NO_3^- and SO_4^{2-}). The usually observed decreasing degradation rate with depth in sediments is not necessarily caused by less efficient electron acceptors in the deeper anoxic layers, but rather by the decreasing quality of organic matter (liability or degradability) and metabolite exchange with depth (Canfield, 1994).

Hulthe et al.(1998) and Kristensen et al. (1995) showed that there is hardly any difference in the degradation rate of fresh organic matter under oxic or anoxic

conditions. Occasionally, degradation of fresh organic matter occurs faster in anoxic than in oxic environments (Hulthe et al., 1998). Older organic matter (or partly degraded materials) however, is degraded faster in an oxic than in an anoxic environment (Hulthe et al., 1998). The most efficient degradation of organic matter occurs when sediments are successively exposed to oxic and anoxic conditions, suggesting that (a part of) the organic products of oxic mineralization can be consumed by anoxic bacteria and vice versa (Hulthe et al., 1998). After several of these cycles the greater amount of organic matter is mineralized, the sediments with the (more refractory) remainder of the organic matter reach their final destination and become buried (de Haas et al., 2002). It has been suggested that the rate of decay under different redox conditions depends primarily on the composition, stage of decomposition and origin of the organic matter (Kristensen et al., 1995; Hulthe et al., 1998). Among anaerobic processes, sulfate respiration mediates similar or slightly higher carbon minerlization than nitrate respiration (Kristensen and Holmer, 2001).

With increasing sediment depth, the C/N ratio increased from its lowest value at the surface to a maximum value at 20-30cm depth. Dittmar and Lara (2001) suggested that a rapid initial release of carbon and an enrichment of nitrogen during early degradation of leaf litter occur, before its incorporation into the sedimentary matrix. The subsequent organic matter degradation in the sediment is probably characterized by reduced mineralization rates as evident for almost invariant C/N ratios in the sediment.

Simple organic compounds like SFAA and SMCHO showed no significant difference with depth (Table B.8a,b). This may be due to their high labile nature of these compounds, which undergo degradation as rapidly as they are formed. The existence of free amino acids and carbohydrates in deep layers is an apparent paradox. Skoog and Benner (1997) suggested that low molecular weight organic matter is the product of diagenesis of macromolecular material. Perhaps the residual low molecular weight aldoses in deep sediments are formed through selective preservation of resistant components of biomolecules. Oscillations between oxic and anoxic conditions and corresponding metabolic pathways on timescales of minutes to hours typically occur deep in bioturbated sediments (Forster and Graf, 1992). Active irrigation and particle reworking by the

macroinfauna inject oxygen and other electron acceptors via burrows to anoxic layers and displace particles rapidly between oxic and anoxic layers (Aller et al. 1996). The resulting mosaic of oxic microzones in the otherwise anoxic sediments clearly promotes oxic and suboxic sediment metabolism.

5.2.3 Nutritional Quality of Sedimentary Organic Matter

Mangroves forests, are efficient in retaining nutrients and sustain a high productivity (Kristensen et al., 1995; Alongi, 1996). Mangrove soils are rich in organic matter, but the detritus is relatively nutrient poor and refractory resulting in low net mineralization rates (Kristensen et al., 1992, 1995). The low net rates of mineralization and pools of dissolved nutrients suggest a tight coupling between nutrient assimilation and mineralization (Holmer et al., 2001). Carbon, nitrogen and phosphorus budgets have indicated that mangrove forests export organic matter mainly as mangrove forest litter and import dissolved inorganic nutrients (Kristensen et al., 1995; Alongi, 1996; Ayakai et al., 1998).

Spatial and temporal changes of sedimentary organic matter in mangrove environments affect spatial distribution, metabolism and dynamics of all benthic components, from bacteria to macrofauna (Danovaro et al., 1995; Duineveld et al., 1997). As benthic deposit-feeders achieve their food requirement by ingesting sedimentary OM, quantity and composition of sedimentary OM are of primary importance in determining its food availability to consumers (Graf, 1989). Organic matter in mangrove environments is composed of labile and refractory compounds. The labile fraction primarily consists of simple sugars and proteins that are rapidly mineralised by bacteria and thus potentially available for higher trophic levels (Fichez, 1991; Danovaro et al., 1993). Conversely, the refractory fraction of OM is largely composed of complex macromolecules (like humic and fulvic acids and complex polymers), which are resistant to microbial attack, degrades slowly. (Fabiano and Danovaro, 1994). Fichez (1991) has proposed the term 'complex organic matter'(COM) to define this residual fraction of the organic carbon, which is not accounted for by lipids, proteins and carbohydrates. As food availability is largely dependent upon OM origin and biochemical composition (Tenore and Hanson, 1980), recent studies have estimated the available fraction of sedimentary organic pools through the determination of the main biochemical classes of organic compounds (i.e. carbohydrates, proteins and lipids), which are assumed to be easier

to digest and assimilate (Fichez, 1991; Danovaro et al., 1993; Fabiano et al., 1995; Dell'Anno et al., 2000). Since the relative importance of these biochemical compounds vary in relation to the productivity of the system, the use of biochemical descriptors might provide insights on the trophic potential of benthic environments. The large amount of organic matter reaching the sediments in mangrove areas are expected to induce a significant benthic response (Josenfson and Conley, 1997). This might explain the high abundance and diversity of the fauna in these environments and their importance as nursery areas for a large number of fish and invertebrate species (Adam, 1990). Although there are studies on temporal changes in the biochemical composition of sedimentary organic matter (Danovaro and Fabiano, 1995; Fabiano et al., 1995; Danovaro, 1996), only little is known about mangrove sediments and comprehensive studies are practically nonexistent. The knowledge of temporal changes in quantity and quality of sedimentary organic matter in intertidal environments is essential to gather information on the system productivity, functioning, and benthic efficiency and, in long term, sustainable management. This study was designed to investigate changes on quantity and quality of sedimentary organic matter composition as food available for benthic consumers in relation to spatial and temporal variations and depths into the sediment.

An evaluation of the nutritional value of the sediment was done assuming carbohydrates, proteins and lipids as the more labile compounds of sedimentary OM. The three main biochemical classes were converted to carbon equivalents (Fichez, 1991; Fabiano et al., 1995; Cividanes et al., 2002). The sum of lipid, protein and carbohydrate carbon taken as the sedimentary biopolymeric carbon fraction (SBPC Fichez, 1991; Fabiano and Danovaro, 1994; Fabiano et al., 1995), assumed as a reliable estimate of the labile fraction of total organic matter, i.e., the fraction which was readily available to deposit-feeders. The SBPC: SOC ratio expressed as a percentage was used as a food index. The residual and uncharacterised fraction of the organic carbon (defined here as complex organic carbon, COC; Fichez, 1991) was determined as the difference between total organic carbon (SOC) and SBPC. Protein to carbohydrate ratio (SP: STCHO) were calculated and assumed as estimate of organic material ageing (Fabiano et al., 1997).

The changes with season and station in biochemical variables in surface sediments were assessed by a two way Analysis (Table B.9a,b,c) and that with site, season and depth in core sediments by three-way Anova (Table B.10a,b and c). Spatial and seasonal variation of biochemical constituents are depicted in Figures 6.20 to 6.26 respectively.

SBPC was a minimum during premonsoon for all the three stations (Fig. 6.23). The maximum SBPC mean value was observed at Station 1 in postmonsoon and minimum at Station 3 during premonsoon. Spatial and monthly variations of SBPC is given in (Table A.51). Mean values for each station were 15.02mg/g, 14.50mg/g and 6.28mg/g respectively. Two-way Anova results showed that all the biochemical variables displayed significant differences with stations (Table B.9a,b) and carbohydrates showed significant difference between season. Table B.9b showed significant difference between station for SBPC. Seasonal and temporal variations of SBPC% and COC% showed no significant variation with station and season. Spatial and monthly variations of SBPC% and COC% are showed (in the Tables A.52 and A.53 respectively). Annual mean value of SBPC% for each station (23.13%, 17.62% and 21.37% respectively) indicated that SBPC accounted for a small fraction of the total organic carbon, whereas, COC% represented the largest pool for organic carbon in surface sediments (mean values were 76.87%, 82.38% and 78.63% at Stations 1, 2 and 3 respectively).

Percentages of the biochemical constituents in the present study were higher than those reported for other areas. Fabiano et al. (1995) found labile organic matter, utilized to estimate the food potentially available for benthic consumers, accounted for only a small percentage (on average less than 10%) of total organic C in subtidal sandy sediments of the Ligurian sea (northwestern Mediterranean). Tenore and Hanson (1980) suggested that about 5-15% of sedimentary detritus, depending on the environmental characteristics, is generally available at any time for benthic consumers. Data presented here are consistent with these findings. The findings showed that a significant fraction utilisable by organisms is very low due to the presence of high COC concentration. A similar result is obtained by converting protein content to N equivalents where proteins account for only 44.4%, 33.16% and 52.97% (annual average) of the total nitrogen pool of Stations 1, 2 and 3 respectively. Thus a significant fraction of organic carbon and nitrogen (55.6%,

66.84% and 47.03% at Stations 1, 2 and 3 respectively for complex organic nitrogen, CON, similar term used for nitrogen counter-part) was of less degradable nature, that concentrates mainly in the medium level and in deeper sediment layers. Thus, although large amounts of detrital organic matter were recorded in mangrove areas, this detritus was of low nutritional quality.

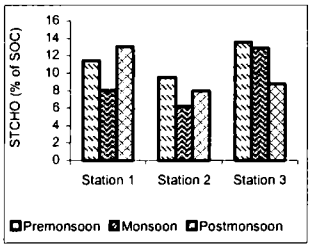


Figure 6.20: Spatial and seasonal variation of carbohydrate-carbon as percentage of organic carbon in surface sediments

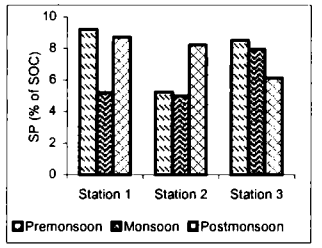


Figure 6.21: Spatial and seasonal variation of protein-carbon as percentage of organic carbon in surface sediments

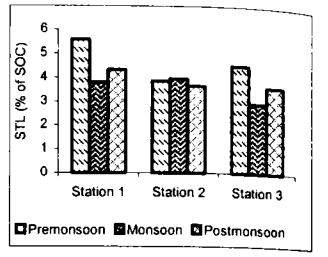


Figure 6.22: Spatial and seasonal variation of lipid-carbon as percentage of organic carbon in surface sediments

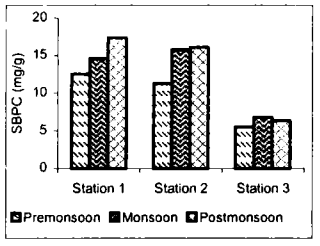


Figure 6.23: Spatial and seasonal variation of biopolymeric carbon in surface sediments

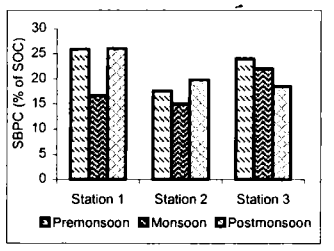


Figure 6.24: Spatial and seasonal variation of biopolymeric carbon as percentage of organic carbon in surface sediments

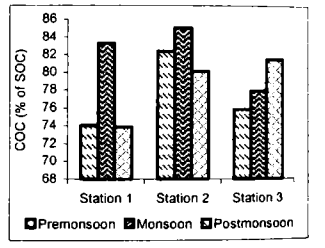


Figure 6.25: Spatial and seasonal variation of complex organic carbon as percentage of organic carbon in surface sediments

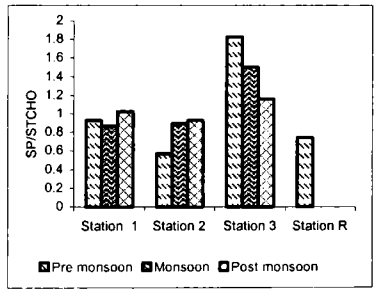


Figure 6.26: Spatial and seasonal variation of protein/ carbohydrate ratio in surface sediments

The biochemical composition of sedimentary OM has recently been used to gather information on the origin, quality and food availability of organic matter (Danovaro et al., 1993; Fabiano et al., 1995; Danovaro, 1996). The high concentrations of sedimentary proteins, carbohydrates and lipids recorded in the study area especially at Stations 1 and 2 are probably related to the morphodynamic, hydrological and physico-chemical characteristics of this sheltered intertidal flat. Low hydrodynamism favours accumulation of OM mainly due to settlement of organic rich fine sediments (Nordstrom, 1992). In addition, the low energy of the mangrove environment of Station 1 and Station 2 allows the formation of fine and stable sediments that permits the settlement of an abundant fauna. All sedimentary labile organic compounds (i.e. carbohydrates, proteins and lipids) were found to vary strongly between sampling periods (even at greater depths), suggesting that mangroves are systems characterised by temporal fluctuations. Spatial and temporal variations of carbohydrates, proteins and lipids showed the same trend with minimum during premonsoon. These variations of the various biochemical compounds suggest marked changes occurred in composition and/or origin of the organic matter inputs during the sampling period. These differences may be related to temperature, grain size, redox potential and water content. Carbohydrate, proteins and lipid percentages showed no significant difference with sediment depth. This is also confirmed by three way-ANOVA (Table B.10a). SBPC% and SP/STCHO ratio also showed no significant difference between depth in core sediments (Table B.10b). This could be due to the accumulation of fresh organic materials like root matter or unutilised organic matter that may become absorbed onto organic macromolecules (Fichez, 1991) or clay minerals. Biochemical composition of sedimentary organic matter seems to be quite different from one marine coastal area to another, but it is usually characterised by small amounts of total lipids and large quantities of proteins and carbohydrate concentrations (Fabiano and Danovaro, 1994). Results of the present study are consistent with this pattern. Carbohydrates were the dominant class among labile compounds [STCHO (% of SBPC) mean values were 47.47%, 45.22% and 43.23% for each station], followed by proteins [SP (% OF SBPC) mean values were 32.12%, 31.55%, and 37.3%] and lipids [STL (% of SBPC) showed annual mean value of 20.4% at Station 1; 23.23% at Station 2,; and 19.45% at Station 3,].

The spatial pattern of organic matter composition in surface sediments showed an inverse relationship between amounts of organic matter and its potential availability to consumers as was reported by Fabiano et al. (1995) as well: low quantities (SOC = 34.4 mg/g) of high-quality organic matter at Station 3 (SBPC% = 24.12%) were replaced by large quantities (SOC = 102mg/g) of low quality material at Station 2 (SBPC% = 19.84%) at Station 2. Sedimentary organic matter at Station 2 was therefore mostly composed of refractory material that was largely unavailable to consumers. Also the analysis of the SP/STCHO ratio supported these conclusions (Table A.54). Increased alteration, particularly at later stages, was generally reflected in decreased percentages of amino acid nitrogen and higher relative non-protein amino acid concentrations. Combined, the measured biochemicals represented important fractions of the organic carbon in all samples. Polysaccharide and protein were also particularly important substrates, and their combined contribution to bulk organic carbon therefore consistently decreased with increased alteration, providing a further index of diagenetic maturity (Cowie, 1991). Since proteins are more readily utilised by bacteria than carbohydrates (Newell and Field, 1983; Ianni, 2000) and are rapidly bound into refractory compounds, low values of SP/STCHO ratio at Station 1 (mean = 0.95) and Station 2 (mean = 0.81) suggest the presence of aged organic matter (Danovaro et al., 1993) and a role of labile proteins as a potentially limiting factor for benthic consumers (Fabiano et al., 1995; Cividanes et al., 2002). SP/STCHO ratio of Station 1 and Station 2 were comparable with that of Station R (mean = 0.74). SP/STCHO ratio was high at Station 3 (mean = 1.5) indicating the presence of newly-produced matter. Thus the sediments of the Station 2 was characterised, most part of the year, by a large amount of aged and/or non-living organic matter and that of Station 3 by fresh organic matter. This might be due to the increased tidal flushing which removes the organic matter as rapidly as it is formed. The sandy nature of the sediment prevents adsorption of organic matter onto the sediment. The SP/STCHO values are comparable to those observed in the Arno Estuary (0.3 to 3.6; Fabiano and Danovaro, 1994) and higher than those reported from the Ligurian Sea (PRT: CHO = 0.14; Fabiano et al., 1995) and from Eastern Mediterranean Sea (PRT: CHO = 0.09; Danovaro et al., 1993), but lower than that in the intertidal flat of Galician coast (below 3.5 to 17.3; Cividanes et al., 2002).

Although SBPC and SOC concentrations at Station 3 were lower than those found at Station 1 and Station 2, the SBPC% was higher at the former **Fig. 6.24**. These results indicate that high SBPC: SOC values are not necessarily associated with large amounts of lipids, proteins and carbohydrates. Thus, though the concentration of biochemical compounds was higher at Station 1 and Station 2, food quality was better at Station 3.

5.2.4 Summary

Mangrove ecosystems in the Cochin area are characterized by their higher fertility and organic productivity than their adjoining estuarine environment. The Aroor mangrove area (Station 3) produces comparatively low organic matter load compared to the Vypin area (Station 1 and Station 2). The results also indicate the role of sediment texture in the preservation and retention of organic matter.

Analysis of elemental and biochemical composition of organic matter showed an inverse relationship between amount of organic matter and its potential availability to consumers; small quantities of high-quality organic matter were replaced by large quantities of refractory material. The different biochemical classes of organic compounds exhibited different spatial patterns. The biopolymeric fraction of organic carbon (i.e. the sum of lipid, carbohydrate and protein carbon) was dominated by carbohydrates followed by proteins, and then lipids in all the three stations. Biopolymeric carbon accounted for only a small fraction of the total organic carbon. Refractory organic carbon (i.e. non biopolymeric) form the major fraction of the total organic carbon. The nutritional quality of the sedimentary organic matter, expressed as the biopolymeric carbon percentage of total organic carbon was higher at Station 3 where also the higher protein to carbohydrate ratio values were observed and related to the presence of newly-produced organic matter. Low biopolymeric carbon percentage of total organic carbon and protein to carbohydrate ratio were recorded at Station 1 and Station 2 compared to Station 3 indicating a low-quality and aged organic matter. Two-way ANOVA in surface sediments suggests no difference between season, which can be attributed to the fact that mangrove detritus provide an eternal supply of organic matter. Three-way analysis in core sediments showed no significant difference with depth.

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Chapter 7

METAL INTERACTION IN MANGROVE SEDIMENT

7.1 Introduction

Metals form an integral part of aquatic systems and no scientific investigations on such systems would be complete without an assessment of the metal interactions. Metals are classified as essential and non essential and derive their importance through their involvement in enzymatic reactions. Often trace quantities of metals regulate physiological processes and decide the health of the system. To supplement the studies on organic constituents investigations on metal concentration was also taken. Discussions have been categorized as been related to alkali and alkaline earth metals as well as those relating to trace/heavy metals. While other areas and adjacent coastal systems have been extensively studied for their geochemistry and sedimentology, this is not the case for the mangroves of Cochin. The purpose of the investigations on sediments was to determine concentration levels and distribution patterns of trace metals and major elements. To fulfil this goal the lateral distribution as well as depth distribution patterns of trace and major elements are presented.

7.2 Surface Sediments

7.2.1 Major Elements

In aquatic sediments, the origin of alkali metals is considered detrital and/or hydrothermal (Sarma and Rao, 1999) and their enrichment is a reflection of the source rock, its weathering, maturity (detrital origin) and hot extraction or basalt precipitation (hydrothermal origin). The alkaline earth metals on the other hand, are influenced by biological enrichment mechanisms. Studies on these metals together can throw light on their relative importance as well as on the interplay of various natural processes (Sarma and Rao, 1999). Na, K, Mg and Ca being major, have received considerable attention in the world oceans including the coastal and offshore sediments of the Indian coasts.

Metals are introduced into estuarine and mangrove environments either in solid/colloidal forms or in solution. Many of the elements have multiple sources and are often associated with more than one host mineral. Reports on the geochemical behavior of Na and K, pertaining to the mangrove environments, are

scarce. Badarudeen (1997) reported the concentrations of sodium (Na) in the sediment cores of Vypin to be in the range from 14mg/g to 45mg/g (av. 29.3mg/g). In the same study, the distribution of potassium (K) in the cores ranged from 10mg/g to 23mg/g (av., 16.3mg/g). Vinithkumar et al. (1999) found Na concentrations in coral reef sediments of Gulf of Mannar biosphere reserve, southeast coast of India, varying between 13.75 to 43.76 mg/g with a mean value of 24.75±5.30mg/g and concentration of K varied from 2.5 to 27 mg/g with a mean value of 12±5.24 mg/g.

- *Sodium (Na)*

Sodium exhibited considerable spatial variation during the study period. Although, Station 3 generally recorded lower values than the other stations, a maximum (15.14mg/g) was observed at this station in August'00 and lowest (0.225mg/g) in October'00 at Station 3 (Table A.55). The annual mean values of each station were 3.31mg/g, 4.24mg/g and 2.01mg/g at Stations 1, 2 and 3 respectively with an overall mean value of 2.98mg/g.

The seasonal fluctuation (Fig. 7.1) showed a minimum at Station 2 during premonsoon and maximum at Station 3 during post-monsoon.

- *Potassium (K)*

As reported for Na, concentrations of K also were low at Station 3 compared to the other two mangrove sites. However, the lowest value (0.092mg/g) was observed at Station 1 in December and the highest (4.90mg/g) concentration was observed at Station 2 in July'00. (Table A.56). Annual mean values were 2.02mg/g, 2.09mg/g and 0.587mg/g at Stations 1 to 3 respectively. At all the three Stations, postmonsoon showed the minimum potassium concentration (Fig. 7.2).

- *Calcium (Ca)*

A maximum concentration of Ca (2.65mg/g) was observed at Station 2 in December'00 and a minimum (0.01mg/g) at Station 3 in the month of February (Table A.57). The mean values of each station were 0.13mg/g, 0.443mg/g and 0.049mg/g for Stations 1 to 3 respectively. A very high peak was observed at Station 2 during postmonsoon and a minimum at Station 3 during premonsoon

(Fig. 7.3). During monsoon, Stations 1 and 2 showed the lowest concentration, but Station 3 showed the peak here.

➢ *Magnesium (Mg)*

In the present study Mg levels varied from 0.001mg/g (August, 00, Station 3) to 15.03mg/g (October'99, Station 1). (Table A.58). The mean values for each station were 5.29mg/g, 6.32mg/g and 1.89mg/g for Stations 1 to 3 respectively. Station 2 showed the highest peak during all the seasons and Station 3 the least, even lower than that of reference site. The trends at Station 1 and Station 2 were similar. All the stations exhibited peak values during monsoon (Fig. 7.4). All the post-monsoon values were at its lowest at all stations.

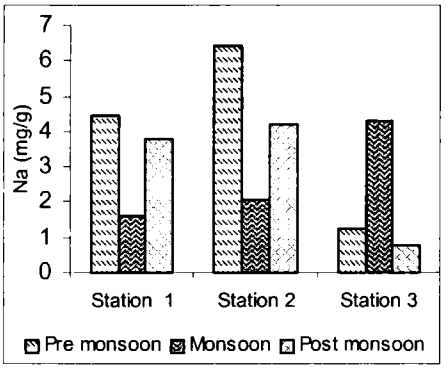


Figure 7.1: Spatial and seasonal variation of sodium in surface sediments

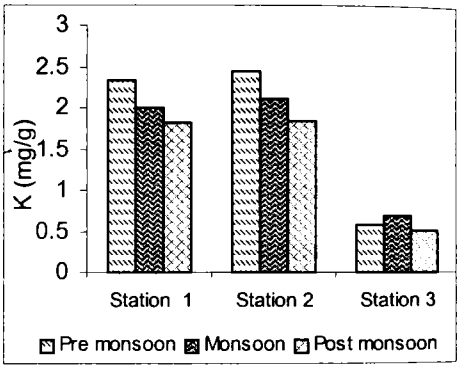


Figure 7.2: Spatial and seasonal variation of potassium in surface sediments

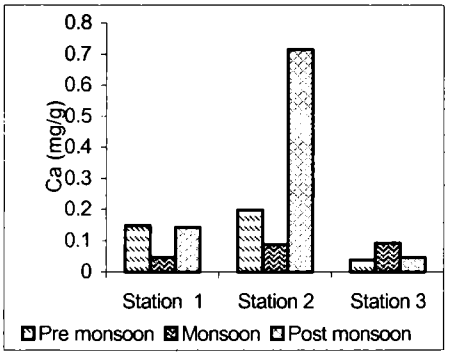


Figure 7.3: Spatial and seasonal variation of calcium in surface sediments

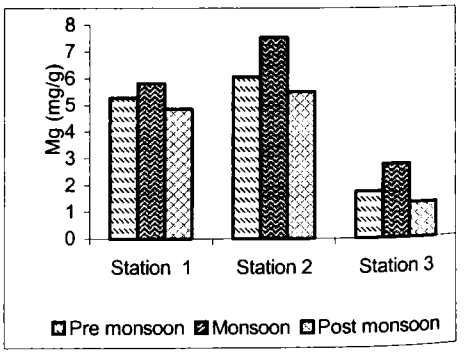


Figure 7.4: Spatial and seasonal variation of magnesium in surface sediments

From the analysis of three mangrove sectors, it is clear that Na accumulation in these environments do not vary much while K displays considerable departures.

ANOVA for K (Table B.11a) showed significant variation between stations and between seasons. Ca showed no significant difference between stations and seasons. But Mg showed significant difference between seasons and stations as evidenced by ANOVA. Na, K, Ca and Mg were very high at Station 1 and Station 2 and very low at Station 3. Differences between soil texture in the three environments revealed that the percentage of silt and clay was higher at Station 1 and Station 2 than at Station 3. In contrast, the percentage of coarse sand was higher at Station 3 than at Station 1 and Station 2. Soil texture also plays a major role in regulating the metal-levels in the sediments, which is evidenced from the present observation that Station 1 and Station 2 contained higher levels of Na, K, Ca and Mg than the Station 3. The high organic matter content at Station 1 and 2 (as compared to that at Station 3) also helped in retaining the metals in the first two stations than the latter. This is also evidenced by the positive correlation of these elements with organic carbon and clay minerals and the negative correlation with sand percentage (Table C.15a-c). Also, the salinity of first two stations was very high, evaporation of dissolved phase leaves a huge content of major elements in sediment. This is evidenced by the significant positive correlation of Na with water salinity. The very low concentrations of Na, K, Ca and Mg at this Station 3 reflect the low salinity at this Station. At Station 3, Na showed no significant correlation with salinity. Na, K, Ca and Mg showed significant positive correlation among themselves (Table C.14a-c and Table C.15a-c) at all stations and during all the seasons. The lower values of K and Mg during postmonsoon at all the three stations could be attributed to the dilution effect by monsoon and postmonsoon rainfall. This is evidenced from their significant positive correlation with salinity of water and chloride content of sediment (Table C.15a-c). In the case of Na no specific seasonal trend was observed.

Tidal incursions of seawater into the mangrove system leads to enrichment of Na and K levels in this area. Enhanced evaporation during summer leads to precipitation and incorporation of these metals into the sediments, explaining the increased concentration of Na and K observed in these mangrove sediments. Adsorption on clay minerals like montmorillionite deposition along with flocs could also account for the above increased metal concentration (Ramanathan et al., 1988). By considering the role of clay minerals in the fixation of Na, it seems that,

the major part of Na in mangrove environments is tied up in montmorillonite/illite. Elevated values of Na over K is due to the ability of the former cation to fix with clay minerals easily (Badarudeen and Sakkir. 1998). Na ions compete very effectively than K ions for the vacant exchange sites in clay minerals. At the same time, being a crucial nutrient element, the mangrove species extent remarkable affinity towards K in the carbohydrate synthesis and for the development of tissues. This process also lowers the K levels in the sediments than Na. In this context, it is clear that the enhanced K content might be derived from the mangrove vegetative debris including the litter fall of the area. The source of K to the sediments is from weathering of rocks rich in orthoclase, microcline and biotite. Considerably reduced concentration of K over Na might be owing to the removal of K by mangrove flora. The high concentration of K at Station 1 and Station 2 could also be due to its easy removal from solution as it gets deposited as flocs after its adsorption on clay minerals. [Sholkovitz, 1978].

The enhanced value of Ca in mangrove sediments might be due to the increased activity of calcareous organisms like crab, mollusks, mussels etc. in this high productive site.

7.2.2 Trace Metals

Industrialization of estuarine areas has generally led to an increase in the metal concentration of aquatic sediments. On release into the aquatic environment metals interact with suspended matter and (depending on the chemical form of the element) are transferred to the sediments by subsequent sedimentation of material.

Mangrove soils were capable of removing pollutants such as Cu, Zn, Cd, P and N from the wastewater (Tam, 1998). Addition of wastewater containing high heavy metal concentrations might have adverse effects on wetland ecosystems, especially the soil microbes (Tam, 1998). The impact of heavy metals on soil microflora has attracted a lot of interest in recent decades as the soil microbes not only constitute the living pool of soil organic matter but are also responsible for an essential part of the major nutrient cycle (Tam, 1998). Heavy metals at high concentrations generally affect the growth, morphology and metabolism of microorganisms in soil (Kandeler et al., 1996), and reduce soil microbial activities including respiration, ammonification, nitrification and enzyme activities (Aoyama

and Nagumo, 1996). Valsecchi et al. (1995) reported that heavy metals appeared to cause an alteration in the soil C cycle, and modify energy metabolism of soil microflora leading to a decrease in the net mineralization of soil organic matter. However other research has shown that heavy metals at low concentrations, or inputs of heavy metals with organic matter, stimulate bacterial growth and population size (Dusek, 1995).

Mangrove ecosystems, being intertidal wetlands, are periodically flooded by incoming and outgoing tides. The ecosystems also receive inputs from fresh water discharge. Thus, their salinities are fluctuating, dependent on the balance between tidal flushing and freshwater inputs (Corredor and Morell, 1994). Variation in salinities might affect the retention of the pollutants. It has been reported that when river water is mixed with sea water, due to the increase in Na, K, Ca. Mg and chloride concentrations, heavy metals could mobilize from soil particulate matter and become dissolved complexes (Comans and Van Dijk, 1998; Paalman et al., 1994). Similarly, Gambrel et al. (1991) reported that the mobilization/ immobilization of trace and toxic metals in brackish marsh soil was affected by salinity. Although increasing salinity led increased soluble Cr and Cu levels, salinity effects on soluble Pb, Ni and Zn were not observed (Tam, 1998).

The elements (Cr, Mn, Fe, Co, Cu, Zn and Pb) were chosen both for their peculiar role in biogeochemical cycles and for their pollutive nature. The coastline is heavily populated with local episodes of chronic pollution. Because the geochemical processes that influence metal accumulation in the environment are reversible it is important to realize that the environment sink of today may become the pollutant source tomorrow. In the present study an attempt is made to quantify the natural and anthropogenic contaminants of toxic heavy metals in the sediment of Cochin mangroves. Because of the distinct changes between seasons there may be seasonal effects on the water table and as a result, there may be some changes in metal distribution. The present study was to determine monthly variations of trace metals such as Fe, Mn, Zn and Cu, in mangrove sediments. It also facilitates the influence of mangrove soils in governing the distribution of metals in their environment.

- *Iron (Fe)*

Fe showed a maximum concentration (37025µg/g) at Station 1 in July'00 and lowest (4.0µg/g) at Station 3 in August'00. The overall mean value was

6970µg/g (Table A.59). The annual mean values were 13432µg/g, 13591µg/g and 4082µg/g at Stations 1, 2 and 3 respectively. The Stations 1 and 2 were significantly higher in Fe concentration, particularly during premonsoon and monsoon season. Seasonal variation (Fig 7.5) showed the highest at Station 2 during monsoon and lowest at Station 3 during postmonsoon. Station 3 showed lower concentrations of Fe. Postmonsoon values showed lowest concentrations at all Stations.

➢ *Chromium (Cr)*

A Maximum Cr concentration (217.7µg/g) was observed in October'00 at Station 1. Cr was not detected at Station 3 in December'99 and January'00 (Table A.60). The annual mean values at Stations 1, 2 and 3 were 100.6µg/g. 102.1µg/g and 41.05µg/g respectively. The seasonal trend was just reverse of that of Iron (Fig. 7.6). Here all the stations showed post-monsoonal peaks and premonsoonal minimum. In the seasonal variation, the maximum concentration was observed at Station 2 during postmonsoon and minimum at Station 3 during pre-monsoon. Here also Station 3 showed the lowest metal concentration comparing the three mangrove stations.

➢ *Manganese (Mn)*

Manganese is a redox-sensitive element and is relatively mobile in aquatic environments. In the present study, Station 2 in September'00 showed the highest concentration of Mn (223µg/g). Mn was not detected at Station 3 in January (Table A.61). The annual mean values for each station were 85.04µg/g, 105.3µg/g and 40.20µg/g at Stations 1, 2 and 3 respectively. In the seasonal data (Fig. 6.7). Station 2 during postmonsoon showed the highest and Station 3 during premonsoon showed the least. Here all the stations showed lowest during premonsoon and Station 3 showed the least Mn concentration. Thus. Mn also behaved similar to Cr and opposite that of Fe.

➢ *Nickel (Ni)*

Nickel showed the highest (317.8µg/g) at Station 2 in September and lowest (zero) at Station 3 in December'99 and January'00 (Table A.62). The mean values at Stations 1, 2 and 3 were 108.5µg/g, 113.2µg/g and 43.12µg/g respectively.

Similar to Cr and Mn and reverse of Fe, Nickel showed maximum in post-monsoon and minimum during premonsoon (Fig. 7.8). Postmonsoon values were significantly higher. During all the seasons, the lowest values were recorded at Station 3. Station 1 and Station 2 showed almost comparable values. The highest peak for Ni was observed at Station 2 during postmonsoon and minimum at Station 3 during premonsoon.

➢ *Copper (Cu)*

Similar to Mn and Ni, highest Cu concentration (110.03μg/g) was observed at Station 2 in September'00 and lowest (2.93μg/g) at Station 3 in December, 99 (Table A.63). The annual mean values for each station were 41.54μg/g, 44.94μg/g and 19.97μg/g at Station 1, 2 and 3 respectively. Similar to Cr, Mn and Ni, copper also showed postmonsoon peak and premonsoon minimum at all the three stations (Fig. 7.9). During all the three seasons Station 3 showed the minimum. During premonsoon Station 3 showed the least and during monsoon at Station 2 showed the peak.

➢ *Zinc (Zn)*

In the present study, Zn levels in the mangrove sediments fluctuated between a minimum (11.04μg/g) at Station 3 in December'99 and maximum (940.5μg/g) at Station 2 in November, 00 (Table A.64). The annual mean values of each station were 146μg/g, 233.1μg/g and 51.44μg/g at Station 1, 2 and 3 respectively. The overall mean value was 139.4μg/g. Similar to Cr, Mn, Ni and Cu and reverse of Fe and Mg, Zinc showed its peak in post-monsoon for all the three stations and minimum during premonsoon (Fig. 7.10). The trend during all the three seasons were Station 2 > Station 1 > Station 3.

➢ *Lead (Pb)*

Pb in mangrove sites was significantly low, with the maximum (126.6μg/g) observed at Station 1 in September'00. Pb was not detected at Station 1 (April,'99), Station 2 (August'99), Station 3 (January'00) and Station 1 and Station 2 (December'99) (Table A.65). The annual mean values were 31.77μg/g, 28.08μg/g and 14.71μg/g respectively for Station 1, 2 and 3. Similar to Cr, Mn, Ni, Cu and

Zn, lead also showed minimum during premonsoon at all the three stations (Fig. 7.11). The Station 3 showed the lowest during all seasons.

➢ *Cobalt (Co)*

Peak Co concentration (73.33μg/g) was observed at Station 1 in October'99 and least (5.81μg/g) at Station 3 in February. The overall mean value was 31μg/g. The annual mean values of each station were 37.42μg/g, 38.44μg/g and 18.80μg/g respectively (Table A.66). Similar to Cr, Mn, Ni, Cu, Zn and Pb, Cobalt also showed premonsoon minimum (Fig 7.12). Station 3 values were lowest during all the three seasons. The values and trends of Station 1 and Station 2 were almost similar. Seasonal variation showed a maximum at Station 2 during monsoon and minimum during premonsoon at Station 3.

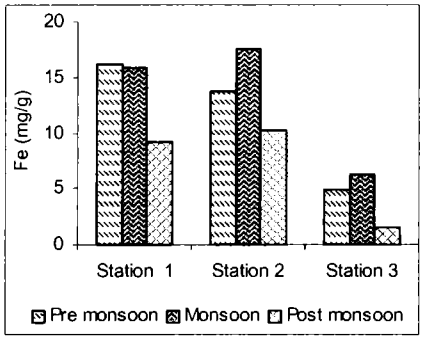


Figure 7.5: Spatial and seasonal variation of iron in surface sediments

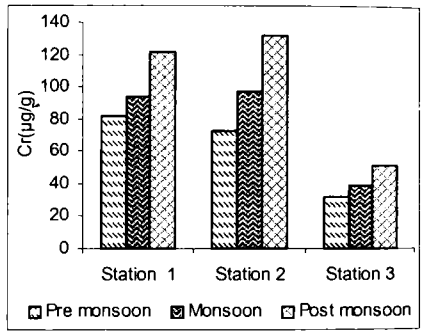


Figure 7.6: Spatial and seasonal variation of chromium in surface sediments

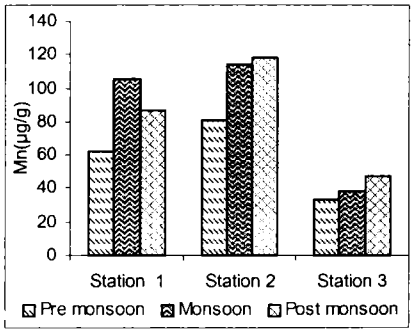


Figure 7.7: Spatial and seasonal variation of manganese in surface sediments

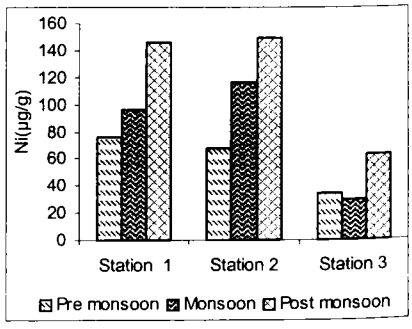


Figure 7.8: Spatial and seasonal variation of nickel in surface sediments

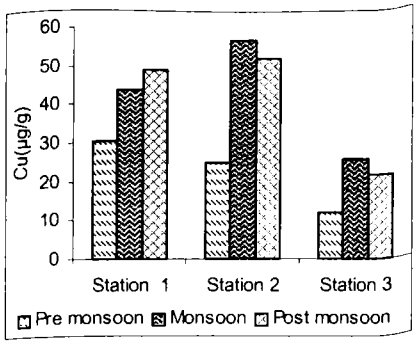


Figure 7.9: Spatial and seasonal variation of copper in surface sediments

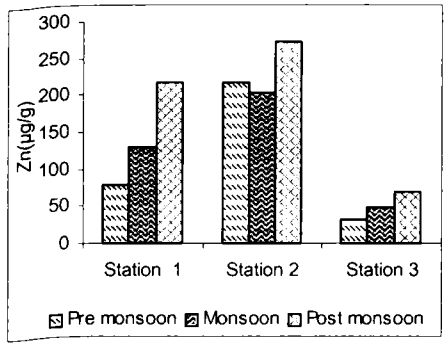


Figure 7.10: Spatial and seasonal variation of zinc in surface sediments

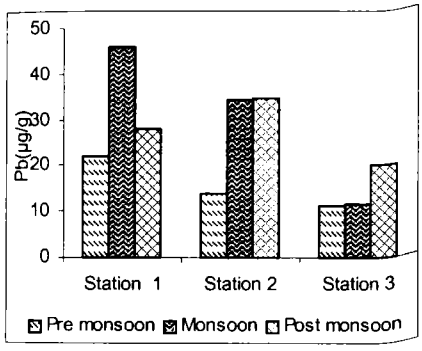


Figure 7.11: Spatial and seasonal variation of lead in surface sediments

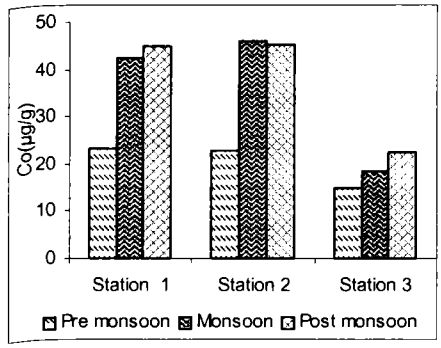


Figure 7.12: Spatial and seasonal variation of chromium in surface sediments

From the concentration of metals it can be concluded that except for Fe (high concentration metal) all the metals showed maximum during postmonsoon and minimum during premonsoon. For Fe, however, the reverse was observed. Station 3 was the least polluted in terms of metal concentration. Except for Pb, all the metals were having significantly higher concentration in the first two-mangrove site, with maximum concentration at Station 2. Only Pb concentrations were significantly lower in the mangrove sites. Anova results showed that the three mangrove areas are playing a significant role in distributing the metals, due to their differential nature of ecosystem and nature of sediments. Statistically significant difference were found during season in metals like Fe, Ni, Cu, Co and Cr (Table B.11b).

Fe is the dominant heavy metal followed by Zn, Mn, Ni, Cr, Pb, Cu and Co. Fe and Mn form complexes with organic compounds in the mangrove

environments (Fe more effectively than Mn) and are thus considerably concentrated in the organic materials. Higher concentration of Fe might be due to the precipitation of iron as sulphide, which is common in mangrove sediments especially at Station 2 due to anoxic condition. These sulphides form a major sink for heavy metals in the mangrove area. Mn is scavenged more effectively by flocculation of hydrophilic organic colloids than by the normal biogeoprocesses of particle formation. Organic particulate matter is responsible for the migration and sedimentation of many inorganic constituents. Moreover, Fe can be absorbed externally into clay minerals or be incorporated into the lattice structure of clay minerals. It is generally conceded that, Mn in sedimentary cycle is leached from the drainage basin as bicarbonates ($MnHCO_3$), but deposited as oxides in the form of organic or inorganic colloids, finely divided detrital grains (Badarudeen, 1997).

Increase of heavy metals in the mangrove sediment is primarily due to the enhanced organic content, abundance of fine particle with greater surface area, precipitation of metals as hydroxide coatings (mainly Fe and Mn) over finely dispersed particles, flocculation due to varying salinity regimes and get deposited along with the surficial sediments. The Stations 1 and 2 are located at short distance in Vypin island and hence showed similar pattern of distribution. Higher concentration of metals at Stations 1 and 2 is because of the clayey nature of sediment that would facilitate higher adsorption of metals. Trace metals were found to be adsorbed onto clay particles due to their high surface to volume ratio and surface charges (Stumm and Morgan, 1981). Upon estuarine mixing, Fe, Mn, organic matter and associated trace metals were flocculated (Sholkovitz, 1976) forming aggregates of several tenths of a micrometer (Mayer, 1982) in size due to reduction in the organic-associated negative charge, primarily by the complexation of divalent cations (Ca and Mg) and subsequent coagulation due to Van der Wall's forces (Sholkovitz, 1976). Finally they are precipitated as Fe-Mn hydrous oxides in the sediments in association with finer fractions of the sediments along with adsorbed trace metals and organic matter (Padma and Periakali, 1999).

Enrichment of metals at Station 2 may also be due to high organic matter load. All the stations throughout the year (in all the season) showed positive correlation with organic carbon and clay percentage and negative relation with sand. In sediments that have an adequate reducing capacity (usually supplied by organic

carbon compounds), redox potential provides an important control on the accumulation of many trace metals (Clark et al, 1997). The redox potential of the sediment can affect metal trapping directly through a change in the oxidation state of the metal itself, or indirectly through a change in the oxidation state of ions that can form complexes with the metal (Clark et al., 1998). In addition, the sharp difference in salinity as the freshwater mixes with seawater would result in the precipitation and coagulation of colloidal clay particles and co precipitation of metal with/or adsorption onto the particles and remove considerable amount of metals from the solution (Senthilnathan and Balasubramanian, 1999) to the sediment.

Higher values of metal concentration were associated with large amount of land and river drainage during the postmonsoon period. Lower levels were observed during premonsoon period due to poor sources and active utilization of metals by organisms. Senthilnathan and Balasubramanian (1999) also observed that all the metals in the surface sediments of estuaries of southeast coast of India were higher during monsoon and lower in summer as observed in the estuaries of southeast coast of India. The higher concentration during postmonsoon could be mainly due to land runoff and influx of metal rich freshwater which in turn reflects in the metal concentration in sediment.

Increased levels of metals (Pb, Zn, and Cr) indicate the influence of industrial discharges, shipping activities and sewage respectively. Lu and Chen (1977) have shown that Cu, Ni, Pb and Zn became relatively static under reducing conditions because of increased organic load and hence accumulated in the sediment. Thus, the industrial complex consisting of fertilizer, refinery, etc., discharging their effluents through monsoon run off via Periyar and Cochin backwaters may influence the water at the mangrove site responsible for the accumulation of heavy metals in sediments. Further, the reduced flushing at Stations 1 and 2 may increase the organic load, leading to settlement of particles in the bottom. High concentration of Zinc may be due to adsorption onto ferromanganese oxides precipitated in sediment (Sarma et al., 1996). Further, organic matter in anoxic sediments in the presence of sulphide ions is a concentrated source of heavy metals (Zn, Pb and Cu) (Nissenbaum and Swaine, 1976). At Station 1 and Station 2, the positive correlations between Ni, Fe, Mn, Cu, Pb, and Cr indicated the enrichment of these metals and adsorption onto

ferromanganese oxides (Sarma et al., 1996). This occurs mostly in Vypin sediment. However, Co and Ni do not correlate with each other indicating their discrete sources or different biogeochemical behaviors. Positive correlations between Cr with Ni and Cu (Table C.14a-c and C.15a-c) showed that these metals are discharged from common source probably through electroplating and port operations. The hydroxides and hydroxy complexes of Cr formed as filaments on shelly materials (Riley and Chester, 1971) and this negatively charged chromium hydroxides act as cation adsorbers (Rutherford, 1977). Thus high correlation between Cr and Cu, Ni may also be due to the adorption capacity of chromium hydroxide for Cu and Ni. At Station 3 almost all metals showed good correlation among themselves indicating their same source and a strong association within the metal-hydroxide coating on grains surfaces which are common in fresh and marine environment (Singh and Subramaniam, 1984).

The higher concentration of zinc and copper would be largely due to the higher levels of these metals in the discharges from agricultural area containing fertilizer, pesticide and rodenticide residues (Senthilnathan and Balasubramanian, 1999). The concentration of lead is low in mangrove environment as the source for these metals is found lacking in the vicinity of study area.

7.3 Core sediments

Metals are initially distributed to surficial sediments of the mangrove ecosystem by surficial waters; most likely rainwater run-off (Saenger et al., 1991). However, these initial distributions of metals in sediments are subsequently modified by seasonal variations in chemical conditions. During the wet season, metals are trapped in surficial sediments. However, during the dry season and, particularly during drought conditions, metals can be mobilized from the surficial sediments and trapped at the water table or moved down the hydraulic gradient. By analyzing cores of undisturbed sediment, it should therefore be possible to reconstruct the "pollution history" of an area. Zwolsman et al. (1993) suggested that metal mobilization is favoured in salt marshes due to a combination of factors, including: the presence of a distinct oxic top layer, acidification in the top layer due to oxidation of iron sulphides and organic matter, high pore water salinities near the surface due to sediment desiccation and periodic shifts from oxidizing to reducing conditions during inundation.

Fig. 7.13 Spatial, seasonal and down core variation of major elements in core sediments

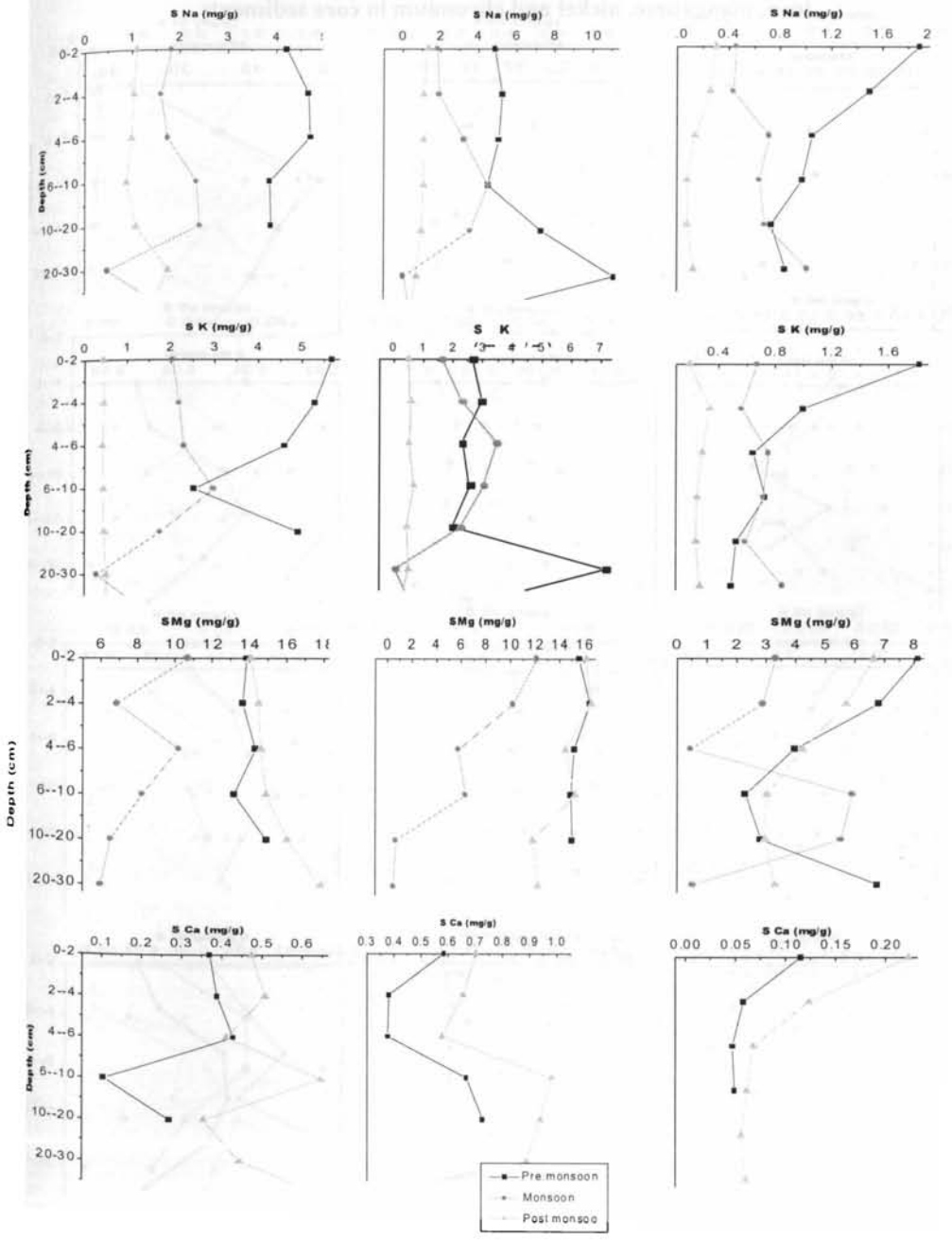
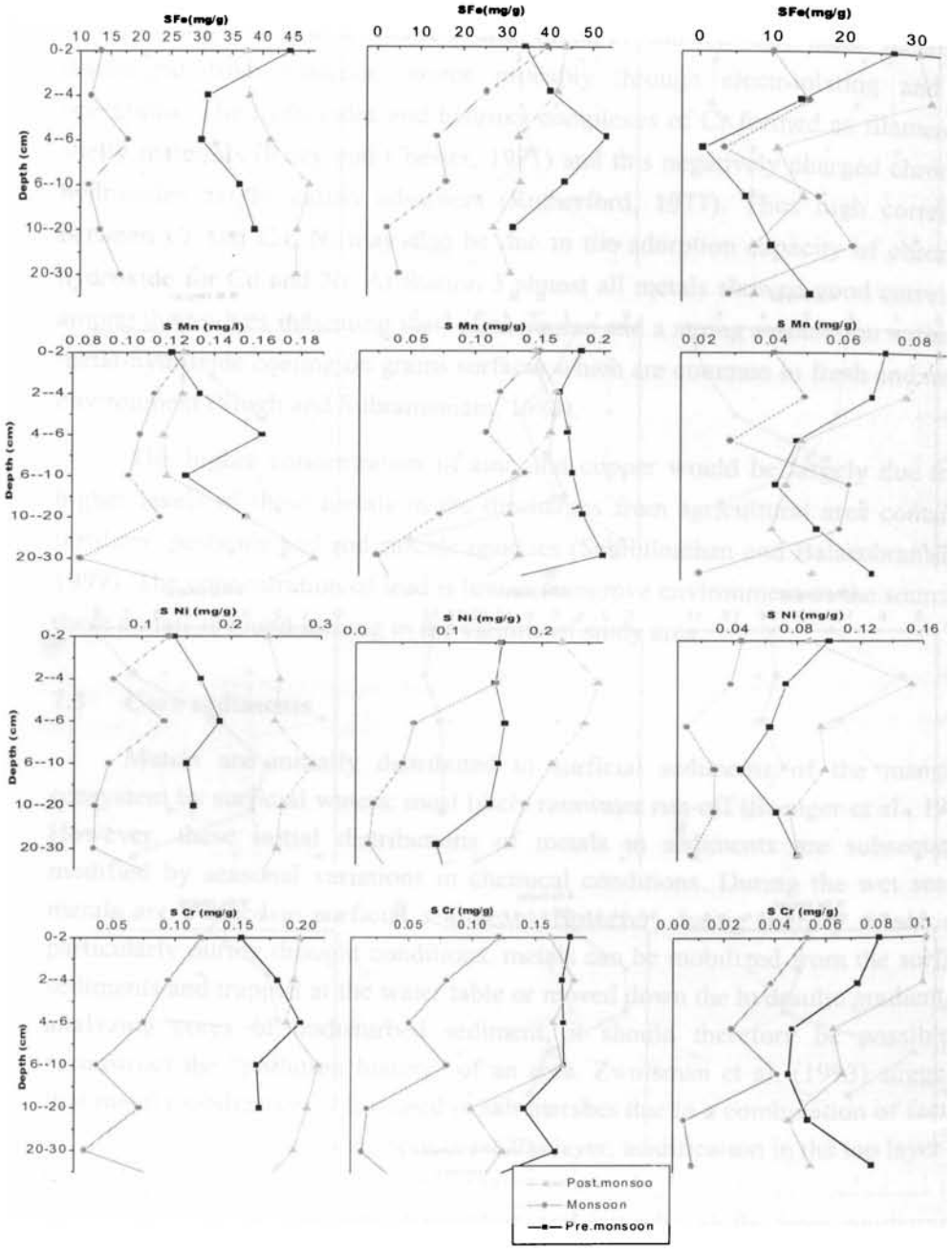
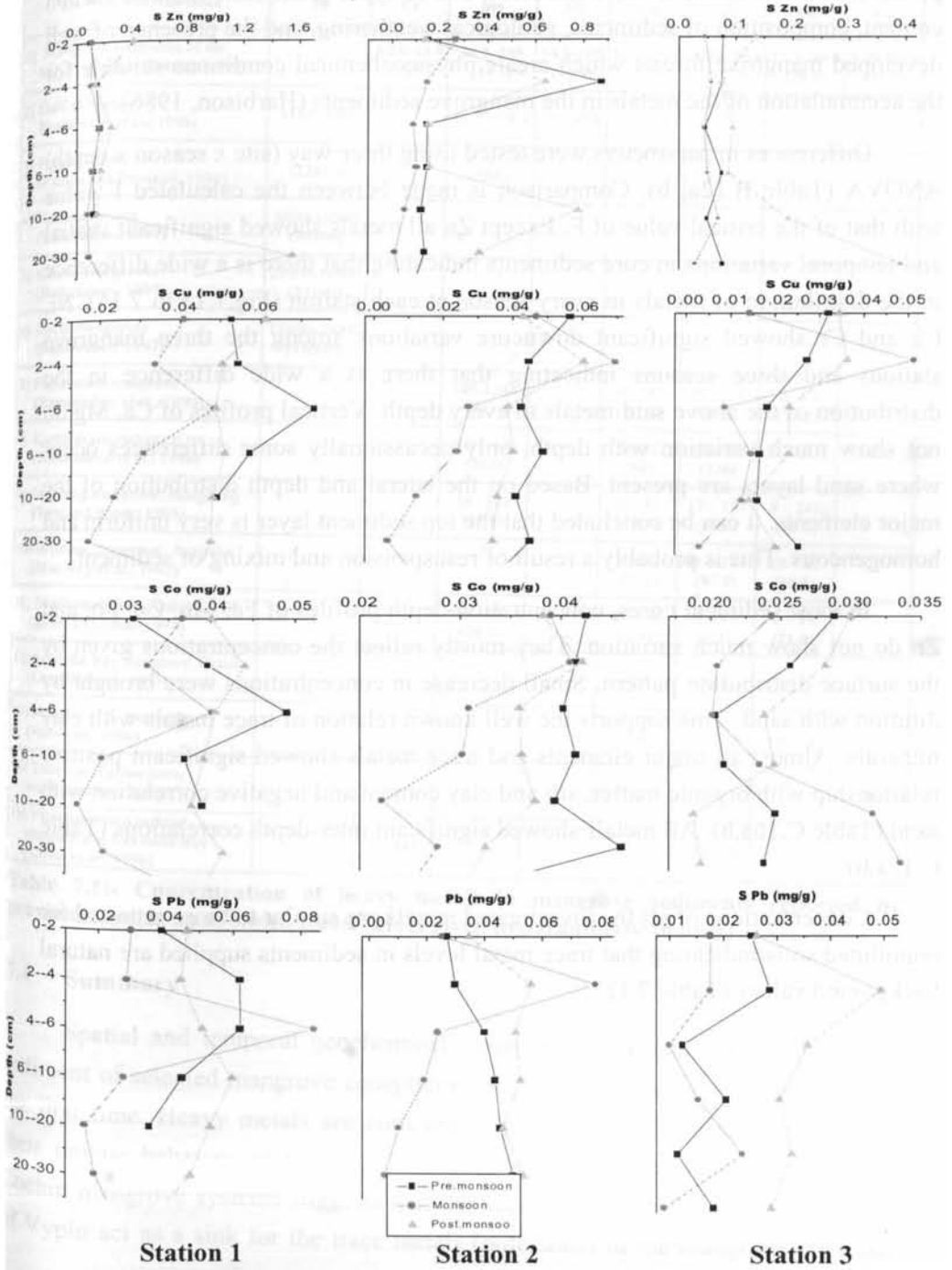


Fig. 7.14 Spatial, seasonal and down core variation of iron, manganese, nickel and chromium in core sediments



Station 1 **Station 2** **Station 3**

Fig. 7.15 Spatial, seasonal and down core variation of zinc, copper, lead and cobalt in core sediments



All metals, except Zn showed high regional variations in their distribution patterns. These variations are considered due to type, grain size, organic carbon content, composition of sediments, geological weathering, and the presence of well developed mangrove forests which create physicochemical conditions suitable for the accumulation of the metals in the mangrove sediments (Harbison, 1986).

Differences in parameters were tested using three way (site x season x depth) ANOVA (Table B.12a, b). Comparison is made between the calculated F value with that of the critical value of F. Except Zn all metals showed significant spatial and temporal variations in core sediments indicating that there is a wide difference in the distribution of metals in every season at each station (Fig.7.13 to 7.15). Ni, Cu and Cr showed significant downcore variations among the three mangrove stations and three seasons indicating that there is a wide difference in the distribution of the above said metals in every depth. Vertical profiles of Ca, Mg do not show much variation with depth, only occassionally some differences occur where sand layers are present. Based on the lateral and depth distribution of the major elements, it can be concluded that the top sediment layer is very uniform and homogeneous. This is probably a result of resuspension and mixing of sediment.

In most sediment cores, concentration-depth profiles of Fe, Mn, Co, Pb, and Zn do not show much variation. They mostly reflect the concentrations given by the surface distribution pattern. Small decrease in concentrations were brought by dilution with sand. This supports the well known relation of trace metals with clay minerals. Almost all major elements and trace metals showed significant positive relationship with organic matter, silt and clay content and negative correlation with sand (Table C.16a,b). All metals showed significant inter-depth correlations (Table C.17a,b).

Concentrations of all the investigated metals are similar to those reported for unpolluted soils indicating that trace metal levels in sediments supplied are natural background values (Table 7.1).

Location and Reference	Fe	Cr	Mn	Ni	Cu	Zn	Pb	Co
1) Mangrove sediments of the U.A.E. shoreline Shriadah (1999)		8.28–18.9 (11.9)	28.8–169 (84.1)	14.8–109 (36.4)	5.31–29.4 (7.21)	4.59–22.4 (11.3)	13.2–49.8 (28.1)	5.70–14.0 (10.2)
2) Gulf of Mannar Kumaresan et al., 1998)	1152–5756		46.2 -128.4	7.5 -19.8	15.2-30.8			
3) Pulicat Lake (Padma and Periakali, 1999).	(22810)		(362)					
4) Veli mangroves (Badarudeen, 1997)	5600-19500 (10100)							
5) Kannur mangroves (Badarudeen, 1997)	23000-54900 (37100)							
6) Kochi mangroves (Badarudeen, 1997)	15600-70000 (45000)							
7) Pichavaram mangrove (Ramanathan et al., 1999)			385-1248 (941)		20 - 81 (43.4)	50 -130 (93)	6 -17 (11.2)	
8) Kumarakam mangrove (Badarudeen et al., 1996)			305 – 645 (452)		19-92 (48)	112-466 (236)		
9) Sai Keng mangrove, Hongkong (Tam and Wong, 1995)			34 –223 (97.9)		1 – 31 (12.4)	17 – 147 (53.3)	8 – 241 (58.2)	
10) Brisbane mangrove, Australia (Mac Key et al., 1992)					3 – 30 (22.4)	41 – 144 (97.9)	20 – 82 (66.8)	
11) Saudi mangrove, Arabian Gulf (Sadiq and Zaidi, 1994)			2 – 69 (28.7)		0.1 – 4 (1.8)	2 – 17 (7.3)	6 – 19 (11.8)	
12) Sepetida Bay mangrove, Brazil (Lacerda et al., 1993)					12.4	311	17.8	
13) Mangrove, S. Australia (Habinson, 1986)					30-80	142-190	85-112	
14) Tuticorin (Palanichamy and Rajendran, 2000)								40
15) Visakhapatnam harbour channels and Kakinada Bay (Sarma et al., 1996).		67-245				231-328		

Table 7.1:- Concentration of heavy metals in mangrove sediments reported by previous studies (range with mean values given in paranthesis, in µg/g)

7.4 Summary

Spatial and temporal geochemical variations of various parameters in the sediment of selected mangrove ecosystems of Cochin were examined in detail for the first time. Heavy metals are enriched in the mangrove sediments, indicating their unique behavior of trapping mechanisms. Heavy metal enrichment in the Cochin mangrove systems suggests that the sediments in this zone especially that of Vypin act as a sink for the trace metals (pollutants) in the mangrove intertidal

sediments, which may pose a threat to mangrove ecosystem in the future. Fairly moderate to good correlation exists between some metals. Thus it is possible that different processes (post depositional mobility, changes in input etc.) operating in the mangrove systems may influence the metal distribution in this environment. Although the heavy metals levels which could affect the health of mangrove plants are not documented in the literature correlations that exist between some heavy metals and organic matter, and grain particles suggest that the mangrove sediments may inevitably become enriched in heavy metals if a source is available. However, minimizing the load of heavy metals discharged into the mangrove ecosystem, particularly those close to urban centres and industrial complexes, is highly recommended.

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Appendix A

SPATIAL AND MONTHLY VARIATIONS

Month	Station 1	Station 2	Station 3	Station R
Apr'99	30	31	**35**	
Aug'99	27	*26*	32	
Oct'99	25	*26*	*26*	
Dec'99	27.5	26.5	30	
Jan'00	28	27.5	31.5	
Feb'00	29	**32**	30	30
Mar'00	30	30.5	30	**32**
Apr'00	**32**	30	30.5	32
May'00	30	30	34	30
July'00	29	31	27	30
Aug'00	29	31	29	30
Sep'00	29	29	30	30
Oct'00	*21*	27	31.5	*29.5*
Nov'00	30	30	29	31
Dec'00	29	29	28	30
Mean	28.37	29.1	30.23	30.45

Table A.1 :- Spatial and monthly variation of temperature(^{0}C)

Month	Station 1	Station 2	Station 3	Station R
Apr'99	7.3	8.6	7.8	
June'99	7.5	**8.8**	7.2	
Aug'99	7.4	7.7	6.9	
Oct'99	*6.8*	7	*6.8*	
Dec'99	7	*6.9*	7.1	
Jan'00	6.9	7.1	7.3	
Feb'00	7.2	8.2	7.6	7.3
Mar'00	6.9	8.2	7	7.6
Apr'00	7.8	8.1	7.4	8.4
May'00	7.55	7.64	7.68	8.24
July'00	**8.12**	7.55	7.54	7.1
Aug'00	7.2	7.3	7.2	7.4
Sep'00	7.9	8.01	7.5	7.3
Oct'00	7.88	8.01	7.17	*6.94*
Nov'00	8.07	8.07	**7.93**	**8.42**
Dec'00	7.35	7.31	7.67	7.9
Mean	7.43	7.78	7.36	7.66

Table A.2 :- Spatial and monthly variation of pH
(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3	Station R
Apr'99	20	21	15	
June'99	23	23	1	
Aug'99	5	6	*0*	
Oct'99	*4*	7	3	
Dec'99	21	22	14	
Jan'00	26.5	24	19	
Feb'00	27.41	30.26	**19.89**	18.16
Mar'00	**28.57**	28.60	14.71	19.87
Apr'00	25.02	24.67	11.95	**21.70**
May'00	10.83	**31.86**	17.52	7.65
July'00	5.10	4.78	2.07	*0.96*
Aug'00	6.37	5.74	3.82	3.51
Sep'00	12.43	12.74	5.42	6.37
Oct'00	8.11	*4.06*	1.16	5.50
Nov'00	14.43	14.82	9.36	12.87
Dec'00	17.94	17.36	11.31	15.99
Mean	15.98	17.37	9.33	11.26

Table A.3 :- Spatial and monthly variation of Salinity(‰)

Month	Station 1	Station 2	Station 3	Station R
Apr'99	1.99	**9.66**	3.50	
June'99	0.79	7.81	6.22	
Aug'99	*0.57*	2.06	4.80	
Oct'99	1.79	2.32	2.68	
Dec'99	0.69	0.77	*1.20*	
Jan'00	1.07	0.71	3.04	
Feb'00	1.64	7.56	1.97	3.29
Mar'00	2.66	4.90	2.38	2.24
Apr'00	3.59	3.28	1.87	3.74
May'00	2.49	no water	**8.93**	2.55
July'00	**6.63**	4.08	4.59	4.08
Aug'00	3.39	*0.52*	3.13	4.70
Sep'00	4.25	no water	5.02	4.75
Oct'00	3.38	2.57	5.47	2.41
Nov'00	4.82	2.89	4.50	*0.22*
Dec'00	1.83	1.33	3.99	**6.99**
Mean	2.60	3.60	3.96	3.50

Table A.4 :- Spatial and monthly variation of Dissolved Oxygen(ml/l)

(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3	Station R
Apr'99	0.473	0.637	0.232	
June'99	0.473	*0.530*	*0.183*	
Aug'99	0.656	0.608	0.232	
Oct'99	*0.251*	1.125	0.232	
Dec'99	0.923	1.292	0.554	
Jan'00	0.964	1.272	0.598	
Feb'00	1.064	1.241	0.650	0.452
Mar'00	1.490	1.555	0.674	0.713
Apr'00	1.820	1.839	0.658	0.736
May'00				
July'00	1.444	2.290	0.673	*0.184*
Aug'00	2.115	2.535	1.729	1.729
Sep'00	**3.268**	**4.177**	**2.445**	2.312
Oct'00	2.700	2.741	2.368	**2.424**
Nov'00	2.574	3.440	2.020	2.106
Dec'00	0.926	0.966	0.584	0.725
Mean	1.409	1.750	0.922	1.265

Table A.5 :- Spatial and monthly variation of Alkalinity(meq/l)

Month	Station 1	Station 2	Station 3	Station R
Apr'99	4.49		4.70	
June'99	0.94	1.36	0.84	
Aug'99	0.84	1.36	0.94	
Oct'99	*0.63*	*0.63*	0.42	
Dec'99	4.80	4.18	2.61	
Jan'00	5.22	5.32	1.98	
Feb'00	4.49	5.53	2.82	2.71
Mar'00	5.74	5.43	**5.32**	2.09
Apr'00	**7.10**	3.97	3.24	4.70
May'00	4.49	**6.37**	3.34	4.80
July'00	1.04	1.04	0.52	*0.42*
Aug'00	1.36	1.36	0.73	0.84
Sep'00	2.09	2.61	1.15	1.46
Oct'00	1.04	1.15	*0.21*	1.15
Nov'00	4.70	5.12	3.03	4.18
Dec'00	5.64	5.74	3.55	**4.91**
Mean	3.41	3.41	2.21	2.72

Table A.6 :- Spatial and monthly variation of Hardness(mg/l)

(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3	Station R
Apr'99	25.86	24.00	47.00	
June'99	45.70	2733.00	**195.60**	
Aug'99	24.93	**6379.00**	73.80	
Oct'99	27.97	21.07	64.14	
Dec'99	17.43	14.31	37.02	
Jan'00	*8.16*	*7.13*	65.14	
Feb'00	41.40	34.60	44.20	23.04
Mar'00	19.40	17.20	*4.40*	31.84
Apr'00	108.82	108.82	76.78	53.20
May'00	**179.00**	360.28	88.97	**88.41**
July'00	55.48	21.56	50.20	47.96
Aug'00	30.60	24.60	102.60	28.40
Sep'00	57.29	110.60	46.12	9.06
Oct'00	38.00	27.16	20.56	*5.43*
Nov'00	17.72	138.16	150.13	8.15
Dec'00	14.33	12.88	21.70	38.36
Mean	44.51	627.15	68.02	33.38

Table A.7 :- Spatial and monthly variation of TSS(mg/l)

Month	Station 1	Station 2	Station 3	Station R
Apr'99	30.67			
June'99	24.43	58.08	**39.97**	
Aug'99		23.80	10.20	
Oct'99	22.85	31.23	7.35	
Dec'99	28.98	22.64	17.46	
Jan'00	6.64	4.29		
Feb'00	17.63	**15.51**	13.30	9.47
Mar'00	18.83	45.08	9.14	43.36
Apr'00	25.67	16.30	7.53	15.35
May'00	**32.57**	13.34	14.96	12.63
July'00	*2.58*	24.82	7.95	11.58
Aug'00	18.52	34.51	16.54	
Sep'00	6.46	28.73	10.66	25.46
Oct'00	6.70	*2.94*	*2.94*	*2.58*
Nov'00	2.58	26.16	33.98	66.11
Dec'00	17.67	15.59	14.01	73.44
Mean	17.52	24.20	14.71	28.89

Table A..8 :- Spatial and monthly variation of dissolved total aminoacids(mg/l)

(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3	Station R
Apr'99	*0.008*			
June'99	0.898	**2.339**	1.073	
Aug'99		1.391	0.245	
Oct'99	2.185	0.785	1.309	
Dec'99	1.579	1.009	1.573	
Jan'00	0.725	0.393		
Feb'00	1.658	0.396	0.367	0.215
Mar'00	0.172	2.037	0.660	0.305
Apr'00	0.132	1.147	*0.108*	0.817
May'00	0.985	0.434	**2.218**	**1.964**
July'00	0.219	*0.223*	0.294	*0.005*
Aug'00	0.279	0.314	0.423	
Sep'00	**3.463**	1.251	0.550	1.454
Oct'00	0.311	0.601	0.388	0.298
Nov'00	0.313	0.620	0.126	0.179
Dec'00	0.927	0.647	1.119	0.456
Mean	0.924	0.906	0.747	0.632

Table A..9 :- Spatial and monthly variation of dissolved free aminoacids(mg/l)

Month	Station 1	Station 2	Station 3	Station R
Apr'99	30.66			
June'99	23.54	55.74	**38.90**	
Aug'99		22.41	9.96	
Oct'99	20.66	30.45	6.05	
Dec'99	27.40	21.63	15.89	
Jan'00	5.92	3.90		
Feb'00	15.98	**15.11**	12.93	9.26
Mar'00	18.66	43.04	8.48	43.06
Apr'00	25.53	15.15	7.42	**14.53**
May'00	**31.59**	12.90	12.74	10.67
July'00	2.36	24.60	7.66	11.57
Aug'00	18.24	34.20	16.12	
Sep'00	3.00	27.48	10.11	24.00
Oct'00	6.38	*2.34*	*2.55*	*2.29*
Nov'00	*2.27*	25.54	33.85	65.93
Dec'00	16.74	14.94	12.89	72.98
Mean	16.60	23.29	13.97	28.25

Table A. 10 :- Spatial and monthly variation of dissolved combined amino acids(mg/l)

(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3	Station R
Apr'99	20.296	19.232	11.996	
June'99	7.315	*3.484*	*0.079*	
Aug'99	*0.718*	4.761	1.569	
Oct'99	3.484	*3.484*	*0.079*	
Dec'99	21.351	20.788	**14.692**	
Jan'00	4.998	2.164	14.563	
Feb'00	14.383	14.076	10.454	8.029
Mar'00	17.531	**27.329**	7.624	21.263
Apr'00	24.807	14.235	6.513	13.444
May'00	**28.032**	8.445	11.545	7.229
July'00	1.834	9.507	6.161	*0.085*
Aug'00	5.469	4.123	1.656	6.142
Sep'00	9.507	18.032	8.610	10.629
Oct'00	5.750	1.507	1.712	1.591
Nov'00	1.005	23.389	13.769	21.415
Dec'00	15.772	13.548	10.564	**22.753**
Mean	11.391	11.756	7.599	11.258

Table A. 11 :- Spatial and monthly variation of Dissolved Proteins(mg/l)

Month	Station 1	Station 2	Station 3	Station R
Apr'99	5.072	4.953	5.670	
June'99	11.527	**21.669**	8.180	
Aug'99	9.495	11.168	4.886	
Oct'99	**13.439**	6.268	5.192	
Dec'99	3.908	4.071	2.441	
Jan'00	3.419	5.537	5.374	
Feb'00	8.948	9.553	8.040	9.755
Mar'00	5.169	4.382	3.594	4.503
Apr'00	1.779	2.310	0.851	*0.586*
May'00	2.301	8.497	*0.783*	**22.281**
July'00	1.163	2.301	6.474	0.656
Aug'00	1.163	2.680	1.795	0.783
Sep'00	1.795	9.509	2.048	2.174
Oct'00	7.233	3.439	**13.935**	3.818
Nov'00	2.933	4.451	4.957	0.657
Dec'00	*1.036*	*1.036*	1.289	1.289
Mean	5.024	6.364	4.719	4.650

Table A.12 :- Spatial and monthly variation of dissolved monosaccharides(mg/l)

(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3	Station R
Apr'99	11.77	15.47	19.77	
June'99	3.64	32.09	30.41	
Aug'99	9.02	*3.28*	9.76	
Oct'99	4.36	5.79	12.84	
Dec'99	9.43	7.81	11.04	
Jan'00	17.09	18.50	18.50	
Feb'00	16.61	18.02	10.46	15.00
Mar'00	*3.59*	29.59	*3.35*	*3.65*
Apr'00	9.02	9.81	7.42	8.09
May'00	15.96	17.60	55.41	29.11
July'00	52.50	41.00	19.88	19.88
Aug'00	31.51	32.66	33.66	7.16
Sep'00	41.00	42.89	28.86	30.75
Oct'00	28.15	20.89	20.00	52.63
Nov'00	30.75	18.87	56.30	4.96
Dec'00	**71.85**	**71.85**	**75.90**	**88.04**
Mean	22.26	24.13	25.85	25.93

Table A.13 :- Spatial and monthly variation of dissolved polysaccharides(mg/l)

Month	Station 1	Station 2	Station 3	Station R
Apr'99	*0.017*	0.196	*0.091*	
June'99	0.353	0.752	0.101	
Aug'99	0.049	0.910	0.092	
Oct'99	1.004	0.574	0.374	
Dec'99	0.626	0.416	0.532	
Jan'00	0.595	*0.096*	0.437	
Feb'00	0.125	0.175	0.336	*0.091*
Mar'00	0.248	0.721	0.227	0.563
Apr'00	0.602	0.336	0.405	0.344
May'00	1.169	0.721	0.545	0.657
July'00	**4.298**	0.375	0.612	0.382
Aug'00	0.433	1.911	0.401	0.286
Sep'00	0.375	**4.738**	0.446	**0.753**
Oct'00	1.496	0.778	**0.787**	0.343
Nov'00	0.388	0.234	0.484	0.458
Dec'00	0.337	0.215	0.337	0.426
Mean	0.757	0.822	0.388	0.430

Table A.14:- Spatial and monthly variation of dissolved total lipids(mg/l)

(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3	Station R
Apr'99	0.534	*0.382*	0.306	
June'99	1.406	**2.586**	*0.231*	
Aug'99	1.318	2.261	0.375	
Oct'99	**2.820**	0.966	0.890	
Dec'99	1.607	2.057	0.858	
Jan'00	*0.461*	0.829	**0.999**	
Feb'00	2.616	1.340	0.858	0.943
Mar'00	0.983	1.287	0.374	0.399
Apr'00	0.945	1.452	0.293	*0.112*
May'00	1.142	1.488	0.451	**1.537**
July'00	0.772	0.945	0.846	0.698
Aug'00	1.019	1.513	0.302	0.278
Sep'00	0.895	1.315	0.401	0.549
Oct'00	1.389	2.130	0.574	0.426
Nov'00	0.722	0.920	0.475	0.401
Dec'00	0.846	0.871	0.302	0.302
Mean	1.217	1.396	0.533	0.564

Table A.15:- Spatial and monthly variation of dissolved tannin and lignin(mg/l)

Month	Station 1	Station 2	Station 3	Station R
Apr'99	6.83	6.02	*1.66*	
June'99	10.13	12.34	3.58	
Aug'99	10.37	10.95	3.82	
Oct'99	10.34	9.37	4.53	
Dec'99	5.82	8.59	2.31	
Jan'00	7.30	8.31	3.39	
Feb'00	9.52	9.08	9.09	4.71
Mar'00	**18.68**	14.88	8.70	2.07
Apr'00	12.41	11.75	**9.90**	2.02
May'00	9.26	**28.45**	3.01	4.26
July'00	12.24	7.48	6.93	2.04
Aug'00	6.35	12.80	4.74	1.96
Sep'00	10.86	11.54	5.63	2.04
Oct'00	11.65	13.22	2.93	**4.83**
Nov'00	6.64	8.23	2.70	*1.62*
Dec'00	*4.99*	*5.00*	2.73	1.86
Mean	9.59	11.13	4.73	2.74

Table A.16:- Spatial and monthly variation of dissolved humic substances(mg/l)

(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3	Station R
Dec'99	**35.21**	24.65	**31.69**	
Jan'00	3.09	4.85	7.06	
Feb'00	3.59	6.42	4.09	2.10
Mar'00	15.54	13.91	8.18	18.00
Apr'00	8.18	12.68	6.95	6.14
May'00	28.12	17.19	12.50	**18.75**
July'00	5.00	4.37	3.12	1.25
Aug'00	3.12	*2.50*	*1.87*	2.50
Sep'00	4.69	**38.28**	3.12	2.50
Oct'00	12.19	3.12	2.50	*0.94*
Nov'00	*2.81*	6.25	5.62	6.56
Dec'00	7.19	*2.50*	4.37	4.06
Mean	10.73	11.39	7.59	6.28

Table A.17:- Spatial and monthly variation of particulate organic carbon(mg/l)

Month	Station 1	Station 2	Station 3	Station R
Dec'99	0.592	0.801	0.202	
Jan'00	0.674	0.478	0.558	
Feb'00	0.364	0.367	0.204	0.136
Mar'00	0.574	0.776	0.120	0.116
Apr'00	0.111	0.209	*0.048*	*0.038*
May'00	**1.478**	0.460	**0.898**	**0.799**
July'00	0.089	0.230	0.205	0.187
Aug'00	0.205	0.180	0.201	0.110
Sep'00	0.172	**1.083**	0.267	0.225
Oct'00	0.253	0.113	0.112	0.180
Nov'00	0.081	*0.104*	0.078	0.238
Dec'00	*0.064*	0.169	0.105	0.144
Mean	0.388	0.414	0.250	0.217

Table A.18 :- Spatial and monthly variation of particulate free aminoacids(mg/l)

Month	Station 1	Station 2	Station 3	Station R
Dec'99	0.420	0.301	0.493	
Jan'00	*0.101*	0.929	0.131	
Feb'00	0.640	0.586	*0.129*	0.378
Mar'00	0.474	1.112		0.230
Apr'00	0.816	**2.384**	0.407	**0.415**
May'00		2.007		
July'00	0.965	0.238	0.347	0.161
Aug'00	0.416	0.365	0.398	
Sep'00	0.907	1.775	0.224	**0.399**
Oct'00	**1.098**	0.428	0.374	0.188
Nov'00	0.618	1.054	**0.568**	0.153
Dec'00	0.278	*0.112*		*0.146*
Mean	0.612	0.941	0.341	0.259

Table A.19:- Spatial and monthly variation of particulate combined amino acids(mg/l)

Month	Station 1	Station 2	Station 3	Station R
Dec'99	1.012	1.101	**0.695**	
Jan'00	0.775	1.406	0.690	
Feb'00	1.004	0.953	*0.333*	0.514
Mar'00	1.048	1.888		0.346
Apr'00	0.927	2.593	0.455	0.454
May'00		2.468		**0.799**
July'00	1.054	0.468	0.552	0.348
Aug'00	0.621	0.545	0.599	*0.110*
Sep'00	1.079	**2.857**	0.491	0.624
Oct'00	**1.351**	0.540	0.486	0.368
Nov'00	0.699	1.158	0.646	0.392
Dec'00	*0.343*	*0.281*		0.290
Mean	0.901	1.355	0.550	0.424

Table A.20:- Spatial and monthly variation of particulate total aminoacids(mg/l)
(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3	Station R
Dec'99	0.405	0.263	**0.456**	
Jan'00	*0.020*	*0.028*	0.040	
Feb'00	0.030	0.392	0.066	0.037
Mar'00	0.094	0.247	0.158	*0.017*
Apr'00	0.256	0.494	0.097	0.076
May'00	0.682	1.451	*0.009*	0.233
July'00	0.172	0.127	0.132	0.132
Aug'00	0.154	0.240	0.334	**0.284**
Sep'00	0.482	**1.586**	0.199	0.257
Oct'00	**0.989**	0.322	0.338	0.186
Nov'00	0.406	0.513	0.298	0.136
Dec'00	0.244	0.087	0.208	0.136
Mean	0.328	0.479	0.195	0.149

Table A.21 :- Spatial and monthly variation of particulate proteins(mg/l)

Month	Station 1	Station 2	Station 3	Station R
Dec'99	1.489	0.919	1.420	
Jan'00	*0.417*	0.706	0.672	
Feb'00	0.589	0.865	0.625	0.249
Mar'00	0.860	1.017	0.757	0.499
Apr'00	1.345	1.796	0.934	1.058
May'00	**2.652**	4.426	**3.129**	**2.185**
July'00	1.218	0.992	0.127	0.486
Aug'00	0.526	0.506	*0.028*	0.383
Sep'00	0.489	**5.120**	0.530	0.279
Oct'00	2.133	*0.122*	0.308	*0.116*
Nov'00	0.743	1.228	0.695	0.316
Dec'00	0.582	0.517	0.520	1.053
Mean	1.087	1.518	0.812	0.662

Table A.22 :- Spatial and monthly variation of particulate total carbohydrates(mg/l)
(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3	Station R
Dec'99	0.575	0.555	0.398	
Jan'00	0.370	0.306	0.530	
Feb'00	0.579	0.434	0.081	0.157
Mar'00	0.724	0.728	0.265	0.378
Apr'00	0.724	0.952	0.470	0.812
May'00	**1.870**	**2.170**	**0.925**	0.785
July'00	0.326	0.269	0.029	0.141
Aug'00	*0.233*	0.385	*0.020*	0.197
Sep'00	0.237	0.935	0.294	0.193
Oct'00	0.659	*0.091*	0.146	*0.088*
Nov'00	0.282	0.290	0.438	0.161
Dec'00	0.282	0.213	0.133	**0.888**
Mean	0.572	0.611	0.311	0.380

Table A.23:- Spatial and monthly variation of particulate monosaccharides(mg/l)

Month	Station 1	Station 2	Station 3	Station R
Dec'99	0.914	0.364	1.022	
Jan'00	0.047	0.401	0.142	
Feb'00	*0.010*	0.431	0.544	0.092
Mar'00	0.137	0.289	0.491	0.121
Apr'00	0.622	0.844	0.464	0.246
May'00	0.782	2.256	**2.203**	**1.401**
July'00	0.892	0.723	0.097	0.345
Aug'00	0.293	0.121	*0.008*	0.186
Sep'00	0.252	**4.185**	0.237	0.086
Oct'00	**1.473**	*0.031*	0.162	*0.028*
Nov'00	0.461	0.939	0.257	0.155
Dec'00	0.301	0.304	0.387	0.165
Mean	0.515	0.907	0.501	0.282

Table A.24:- Spatial and monthly variation of particulate polysaccharides(mg/l)
(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3	Station R
Dec'99	**1.371**	0.283	0.218	
Jan'00	*0.003*	0.200	0.581	
Feb'00	0.099	0.814	0.232	0.132
Mar'00	0.178	0.530	0.401	*0.028*
Apr'00	0.487	1.177	*0.089*	0.150
May'00	1.182	0.724	**1.192**	**1.162**
July'00	0.347	0.913	0.538	0.309
Aug'00	0.227	*0.126*	0.165	0.282
Sep'00	0.357	**9.311**	0.154	0.264
Oct'00	0.645	0.355	0.211	0.181
Nov'00	0.219	0.408	0.152	0.211
Dec'00	0.169	0.142	0.284	0.201
Mean	0.440	1.249	0.351	0.292

Table A.25:- Spatial and monthly variation of particulate total lipids(mg/l)
(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3	Station R
Dec'99	0.076	0.105	**0.228**	
Jan'00	*0.032*	0.074	0.126	
Feb'00	0.037	*0.054*	0.139	0.026
Mar'00	0.185	0.185	0.160	0.060
Apr'00	0.220	0.293	0.109	0.028
May'00	**0.384**	0.709	0.193	**0.293**
July'00	0.091	0.122	0.151	0.029
Aug'00	0.059	0.210	*0.065*	0.039
Sep'00	0.144	**2.747**	0.081	0.033
Oct'00	0.334	0.158	0.077	*0.014*
Nov'00	0.072	0.131	0.081	0.028
Dec'00	0.046	0.070	0.085	0.037
Mean	0.140	0.405	0.124	0.058

Table A.26:- Spatial and monthly variation of particulate tannin and lignin(mg/l)
(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3	Station R
Dec'99	0.827	1.150	**3.170**	
Jan'00	*0.409*	*0.910*	1.468	
Feb'00	1.603	1.948	2.910	*0.208*
Mar'00	1.208	1.704	1.872	0.340
Apr'00	1.590	2.068	1.559	0.402
May'00	**3.736**	4.791	1.376	**2.496**
July'00	1.717	1.869	1.890	0.248
Aug'00	1.315	1.310	1.249	0.445
Sep'00	1.704	**7.465**	1.123	0.384
Oct'00	2.750	1.922	1.533	0.373
Nov'00	1.177	2.322	1.229	0.449
Dec'00	0.928	1.262	*0.951*	0.539
Mean	1.580	2.393	1.694	0.588

Table A.27:- Spatial and monthly variation of particulate humic substances(mg/l)
(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3	Station R
Dec'99	0.575	0.533	0.720	
Jan'00	0.319	*0.292*	0.287	
Feb'00	0.419	3.051	0.813	0.880
Mar'00	*0.301*	0.889	0.968	*0.047*
Apr'00	1.564	1.948	0.699	0.618
May'00	1.212	4.222	*0.034*	0.621
July'00	1.722	1.456	2.109	5.273
Aug'00	2.467	4.790	**8.899**	5.689
Sep'00	5.140	8.342	3.186	5.149
Oct'00	4.057	**8.355**	6.765	**9.906**
Nov'00	**7.210**	4.106	2.647	1.039
Dec'00	1.698	1.740	2.379	1.678
Mean	2.224	3.310	2.459	3.090

Table A.28 : Spatial and monthly variation of particulate Protein-carbon percentage of organic carbon

(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3	Station R
Dec'99	*1.69*	*1.49*	1.79	
Jan'00	5.41	5.82	3.81	
Feb'00	6.56	5.39	6.12	4.74
Mar'00	2.21	2.92	3.70	*1.11*
Apr'00	6.58	5.67	5.38	6.90
May'00	3.77	**10.30**	**10.01**	4.66
July'00	9.74	9.07	1.62	**15.56**
Aug'00	6.73	8.10	*0.60*	6.13
Sep'00	4.17	5.35	6.79	4.46
Oct'00	7.00	1.56	4.93	4.95
Nov'00	**10.57**	7.86	4.94	1.92
Dec'00	3.24	8.28	4.75	10.37
Mean	5.64	5.98	4.54	6.08

Table A.29 : Spatial and monthly variation of particulate Carbohydrate-carbon percentage of organic carbon

Month	Station 1	Station 2	Station 3	Station R
Dec'99	3.270	*0.963*	*0.578*	
Jan'00	*0.068*	3.463	6.912	
Feb'00	2.326	10.643	4.774	5.269
Mar'00	0.964	3.203	4.118	*0.129*
Apr'00	5.003	7.795	1.071	2.050
May'00	3.530	3.539	8.009	5.207
July'00	5.828	17.534	**14.468**	**20.795**
Aug'00	6.089	4.230	7.408	9.468
Sep'00	6.393	**20.434**	4.127	8.871
Oct'00	4.445	9.538	7.080	16.232
Nov'00	**6.530**	5.484	2.263	2.697
Dec'00	1.979	4.761	5.448	4.154
Mean	3.869	7.632	5.521	7.487

Table A.30 : Spatial and monthly variation of Particulate Lipid-carbon percentage of organic carbon

(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3	Station R
Dec'99	1.949	0.736	0.979	
Jan'00	*0.179*	0.465	0.777	
Feb'00	0.334	1.226	0.479	*0.229*
Mar'00	0.541	0.976	0.719	0.231
Apr'00	1.075	1.954	0.497	0.587
May'00	**2.394**	3.104	**2.257**	**1.967**
July'00	0.865	1.228	0.569	0.520
Aug'00	0.478	0.428	*0.317*	0.532
Sep'00	0.736	**10.563**	0.441	0.462
Oct'00	1.889	0.508	0.469	0.291
Nov'00	0.683	1.091	0.554	0.371
Dec'00	0.497	0.369	0.550	0.658
Mean	0.968	1.887	0.717	0.585

Table A.31:- Spatial and monthly variation of Particulate Biopolymeric carbon

Month	Station 1	Station 2	Station 3	Station R
Dec'99	5.54	*2.99*	*3.09*	
Jan'00	5.80	9.58	11.01	
Feb'00	9.31	19.08	11.71	10.89
Mar'00	*3.48*	7.02	8.79	*1.28*
Apr'00	13.15	15.41	7.15	9.57
May'00	8.51	18.06	18.06	10.49
July'00	17.29	28.06	18.20	**41.63**
Aug'00	15.29	17.12	16.91	21.28
Sep'00	15.71	**34.13**	14.10	18.48
Oct'00	15.50	19.46	**18.77**	31.09
Nov'00	**24.30**	17.45	9.85	5.66
Dec'00	6.92	14.78	12.58	16.20
Mean	11.73	16.93	12.52	16.66

Table A.32 : Spatial and monthly variation of Particulate Biopolymeric carbon percentage of organic carbon

(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3	Station R
Dec'99	94.46	**97.01**	**96.91**	
Jan'00	94.20	90.42	88.99	
Feb'00	90.69	80.92	88.29	89.11
Mar'00	**96.52**	92.98	91.21	**98.72**
Apr'00	86.85	84.59	92.85	90.43
May'00	91.49	81.94	81.94	89.51
July'00	82.71	71.94	81.80	*58.37*
Aug'00	84.71	82.88	83.09	78.72
Sep'00	84.29	*65.87*	85.90	81.52
Oct'00	84.50	80.54	*81.23*	68.91
Nov'00	*75.70*	82.55	90.15	94.34
Dec'00	93.08	85.22	87.42	83.80
Mean	88.27	83.07	87.48	83.34

Table A.33 : Spatial and monthly variation of Particulate Complex organic carbon percentage of organic carbon

Month	Station 1	Station 2	Station 3	Station R
Dec'99	0.340	0.358	0.402	
Jan'00	*0.059*	*0.050*	0.075	
Feb'00	0.064	0.567	0.133	0.186
Mar'00	0.136	0.304	0.262	*0.042*
Apr'00	0.238	0.344	0.130	0.090
May'00	0.321	0.410	*0.003*	0.133
July'00	0.177	0.161	1.302	0.339
Aug'00	0.366	0.592	**14.897**	0.928
Sep'00	**1.231**	0.338	0.469	1.154
Oct'00	0.580	**3.295**	1.373	**2.001**
Nov'00	0.682	0.522	0.536	0.540
Dec'00	0.524	0.210	0.501	0.162
Mean	0.393	0.596	1.674	0.557

Table A.34 : Spatial and monthly variation of Protein to Carbohydrate ratio particulate matter.

(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3
Apr'99	51.35	113.87	**84.81**
June'99	80.08	88.85	50.22
Aug'99	66.82	83.58	51.35
Oct'99	49.37	49.67	34.72
Dec'99	47.81	69.67	39.38
Jan'00	51.81	88.71	23.43
Feb'00	*42.04*	*44.94*	24.34
Mar'00	61.25	58.87	14.75
Apr'00	66.85	75.93	17.59
May'00	60.73	64.69	*9.83*
July'00	93.08	93.72	21.81
Aug'00	99.75	95.75	14.66
Sep'00	**105.33**	**152.76**	31.78
Oct'00	85.11	122.12	45.73
Nov'00	97.49	104.46	31.94
Dec'00	84.54	99.05	31.20
Mean	71.46	87.92	32.97

Table A.35:- Monthly variation of sedimentary organic carbon(mg/g)

Season	Station 1	Station 2	Station 3
Premon	*3.03*	*4.42*	1.60
Monsoon	3.32	4.42	**1.82**
Postmon	**3.88**	**4.91**	*1.27*
Mean	3.41	4.58	1.56

Table A.36:- Seasonal variation of sedimentary organic nitrogen(mg/g)

Season	Station 1	Station 2	Station 3
Premon	18.64	16.22	18.88
Monsoon	26.81	23.29	18.65
Postmon	17.86	18.13	27.11
Mean	21.10	19.21	21.55

Table A.37:- Seasonal variation of sedimentary C/N
(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3
Apr'99			
June'99			
Aug'99	32.95	**37.40**	13.21
Oct'99	**35.65**	30.21	8.37
Dec'99	25.16	22.32	11.42
Jan'00	10.36	15.58	10.70
Feb'00	18.97	25.23	9.86
Mar'00	8.66	9.14	9.21
Apr'00	7.08	7.78	*4.42*
May'00	10.81	*7.43*	6.51
July'00	*6.36*	10.01	6.13
Aug'00	11.66	9.11	6.85
Sep'00	13.86	15.05	**16.42**
Oct'00	11.99	13.28	6.11
Nov'00	10.23	10.33	4.53
Dec'00	13.37	17.38	7.20
Mean	15.51	16.45	8.64

Table A.38 :- Monthly variation of sedimentary total aminoacids(mg/g)

Month	Station 1	Station 2	Station 3
Apr'99			
June'99			
Aug'99	0.214	0.329	0.142
Oct'99	0.197	0.393	0.135
Dec'99	0.265	0.406	0.123
Jan'00	0.214	0.263	0.097
Feb'00	0.231	0.350	0.108
Mar'00	0.186	**0.552**	0.074
Apr'00	*0.102*	0.267	0.075
May'00	0.232	*0.181*	*0.038*
July'00	0.291	0.471	0.087
Aug'00	**0.543**	0.362	0.066
Sep'00	0.356	0.530	**0.300**
Oct'00	0.189	0.361	0.184
Nov'00	0.287	0.397	0.200
Dec'00	0.328	0.339	0.199
Mean	0.260	0.372	0.131

Table A.39:- Monthly variation of sedimentary free amino-acids(mg/g)
(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3
Apr'99			
June'99			
Aug'99	32.735	**37.070**	13.066
Oct'99	**35.453**	29.815	8.233
Dec'99	24.898	21.915	11.293
Jan'00	10.143	15.321	10.603
Feb'00	18.741	24.880	9.752
Mar'00	8.477	8.586	9.131
Apr'00	6.982	7.514	4.346
May'00	10.573	*7.254*	6.471
July'00	*6.072*	9.534	6.046
Aug'00	11.114	8.746	6.785
Sep'00	13.503	14.523	**16.122**
Oct'00	11.804	12.915	5.929
Nov'00	9.947	9.931	*4.334*
Dec'00	13.040	17.040	7.005
Mean	15.249	16.075	8.508

Table A.40:- Monthly variation of sedimentary combined aminoacids(mg/g)

Month	Station 1	Station 2	Station 3
Apr'99	14.80	7.68	12.14
June'99	8.43	10.60	**14.64**
Aug'99	15.17	12.21	7.51
Oct'99	8.14	**21.53**	2.82
Dec'99	**22.60**	17.17	6.81
Jan'00	*1.96*	1.40	2.82
Feb'00	16.67	12.21	9.34
Mar'00	2.48	*1.04*	*0.28*
Apr'00	5.53	7.04	4.01
May'00	5.10	4.91	0.75
July'00	5.24	9.09	2.30
Aug'00	6.84	4.23	2.48
Sep'00	6.98	14.50	2.72
Oct'00	11.60	12.46	5.91
Nov'00	9.87	8.06	3.08
Dec'00	11.31	11.13	4.19
Mean	9.55	9.70	5.11

Table A.41:- Monthly variation of sedimentary proteins(mg/g)
(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3
Apr'99	12.75	12.46	2.90
June'99	12.62	11.74	5.05
Aug'99	7.91	9.22	3.36
Oct'99	*6.43*	11.99	2.32
Dec'99	9.39	15.12	2.70
Jan'00	**35.99**	*6.39*	3.75
Feb'00	10.38	14.26	3.96
Mar'00	16.71	9.52	*1.25*
Apr'00	11.75	16.43	9.69
May'00	14.98	16.64	5.46
July'00	14.92	16.18	9.27
Aug'00	20.11	14.21	5.60
Sep'00	33.84	**28.61**	13.23
Oct'00	24.11	25.33	**14.70**
Nov'00	34.18	22.81	12.63
Dec'00	25.88	23.38	9.45
Mean	18.25	15.89	6.58

Table A.42 :- Monthly variation of sedimentary total carbohydrates(mg/g)

Month	Station 1	Station 2	Station 3
Apr'99			
June'99			
Aug'99	*0.163*	0.452	0.149
Oct'99	0.338	0.886	0.037
Dec'99	0.376	0.581	0.299
Jan'00	0.425	*0.187*	0.171
Feb'00	0.408	0.711	0.291
Mar'00	0.245	1.438	0.175
Apr'00	0.272	0.889	0.258
May'00	0.601	0.940	0.517
July'00	0.727	1.094	0.283
Aug'00	1.429	0.900	*0.031*
Sep'00	0.566	1.220	0.501
Oct'00	0.440	0.898	0.495
Nov'00	0.840	**1.814**	0.337
Dec'00	**1.695**	1.722	**0.792**
Mean	0.609	0.981	0.310

Table A.43:- Monthly variation of sedimentary mono-saccharides(mg/g)
(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3
Apr'99			
June'99			
Aug'99	7.74	8.77	3.21
Oct'99	*6.09*	11.11	2.28
Dec'99	9.02	14.54	2.40
Jan'00	**35.56**	*6.20*	3.57
Feb'00	9.97	13.54	3.67
Mar'00	16.47	8.08	*1.07*
Apr'00	11.48	15.54	9.43
May'00	14.38	15.70	4.95
July'00	14.19	15.08	8.98
Aug'00	18.68	13.31	5.57
Sep'00	33.27	**27.39**	12.73
Oct'00	23.67	24.43	**14.21**
Nov'00	33.34	20.99	12.29
Dec'00	24.19	21.66	8.65
Mean	18.43	15.45	6.65

Table A.44:- Monthly variation of sedimentary polysaccharides(mg/g)

Month	Station 1	Station 2	Station 3
Apr'99	5.005	2.266	2.478
June'99	**5.131**	5.421	**2.712**
Aug'99	4.046	3.971	0.718
Oct'99	*1.834*	3.607	0.935
Dec'99	3.519	2.560	1.290
Jan'00	3.564	2.413	1.582
Feb'00	2.795	3.006	1.608
Mar'00	2.661	3.731	1.172
Apr'00	2.403	*1.575*	*0.586*
May'00	3.520	3.778	0.597
July'00	2.597	2.948	0.612
Aug'00	3.266	2.217	0.776
Sep'00	4.327	**10.995**	0.818
Oct'00	3.963	8.067	2.142
Nov'00	4.944	4.066	1.932
Dec'00	2.676	1.993	0.769
Mean	3.516	3.913	1.295

Table A.45 :- Monthly variation of sedimentary total lipids(mg/g)
(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3
Apr'99	4.227	3.137	1.419
June'99	4.311	3.891	1.976
Aug'99	3.949	3.585	1.879
Oct'99	3.358	3.654	1.305
Dec'99	4.019	3.168	*1.221*
Jan'00	4.699	2.944	**2.499**
Feb'00	**6.841**	4.878	1.693
Mar'00	6.140	6.162	1.314
Apr'00	3.865	4.954	1.855
May'00	3.186	*2.630*	1.285
July'00	5.270	**6.330**	2.004
Aug'00	5.423	5.167	1.721
Sep'00	*2.753*	3.330	1.444
Oct'00	3.724		2.362
Nov'00	4.745	3.256	1.937
Dec'00	3.254	3.400	1.507
Mean	4.360	4.033	1.714

Table A.46:- Monthly variation of sedimentary tannin and lignin(mg/g)

Month	Station 1	Station 2	Station 3
Apr'99	3.424	*0.458*	*2.624*
June'99	6.057	18.829	11.830
Aug'99	*1.802*	4.933	7.822
Oct'99	5.665	6.789	10.127
Dec'99	10.159	15.005	8.727
Jan'00	6.631	21.634	**12.699**
Feb'00	5.597	5.687	7.275
Mar'00	**29.987**	30.698	10.511
Apr'00	28.437	**32.117**	11.777
May'00	22.466	26.378	7.114
July'00	27.138	29.433	11.897
Aug'00	26.993	20.641	7.054
Sep'00	20.634	21.697	8.543
Oct'00	18.352	25.060	9.339
Nov'00	17.603	13.840	7.860
Dec'00	10.460	15.408	10.358
Mean	15.088	18.038	9.097

Table A.47:- Monthly variation of sedimentary humic substances(mg/g)
(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3
Apr'99	9.93	4.38	*1.37*
June'99	6.31	5.29	4.02
Aug'99	*4.73*	4.41	2.62
Oct'99	5.21	9.66	2.67
Dec'99	7.86	8.68	2.74
Jan'00	**27.79**	*2.88*	6.39
Feb'00	9.87	**12.69**	6.51
Mar'00	18.96	6.47	3.38
Apr'00	7.03	8.66	22.04
May'00	9.87	10.29	**22.23**
July'00	6.41	6.90	16.99
Aug'00	8.06	5.93	15.28
Sep'00	12.85	7.49	16.65
Oct'00	11.33	8.30	12.86
Nov'00	14.02	8.73	15.81
Dec'00	12.25	9.44	12.11
Mean	10.78	7.51	10.23

Table A.48:- Monthly variation of Carbohydrate carbon percentage of organic carbon in surface sediments

Month	Station 1	Station 2	Station 3
Apr'99	14.41	3.37	7.16
June'99	5.26	5.97	14.58
Aug'99	11.35	7.30	7.31
Oct'99	8.25	**21.67**	4.05
Dec'99	**23.64**	12.33	8.65
Jan'00	*1.89*	*0.79*	6.02
Feb'00	19.83	13.58	**19.18**
Mar'00	3.51	0.88	*0.96*
Apr'00	4.14	4.64	11.39
May'00	4.19	3.79	3.82
July'00	2.81	4.85	5.28
Aug'00	3.43	2.21	8.45
Sep'00	3.31	4.75	4.28
Oct'00	6.81	5.10	6.46
Nov'00	5.06	3.86	4.82
Dec'00	6.69	5.62	6.72
Mean	7.79	6.29	7.45

Table A.49 : Monthly variation of Protein-carbon percentage of organic carbon in surface sediments

(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3
Apr'99	**8.19**	*1.67*	2.45
June'99	5.38	5.13	4.54
Aug'99	5.09	3.99	*1.17*
Oct'99	3.12	**6.10**	2.26
Dec'99	6.18	3.09	2.75
Jan'00	5.78	2.28	5.67
Feb'00	5.58	5.62	5.55
Mar'00	6.34	5.32	**6.68**
Apr'00	3.02	1.74	2.80
May'00	4.87	4.91	5.10
July'00	*2.34*	2.64	2.36
Aug'00	2.75	1.95	4.44
Sep'00	3.45	6.05	2.16
Oct'00	3.91	5.55	3.93
Nov'00	4.26	3.27	5.08
Dec'00	2.66	1.69	2.07
Mean	4.56	3.81	3.69

Table A.50 : Monthly variation of Lipid-carbon percentage of organic carbon in surface sediments

Month	Station 1	Station 2	Station 3
Apr'99	16.70	10.73	9.31
June'99	13.58	14.55	**11.62**
Aug'99	14.15	13.13	5.70
Oct'99	*8.18*	18.59	3.12
Dec'99	18.01	16.78	5.57
Jan'00	18.37	*5.28*	4.24
Feb'00	14.83	14.33	7.60
Mar'00	10.16	7.46	*1.63*
Apr'00	9.48	11.42	6.37
May'00	11.50	12.28	3.06
July'00	10.77	13.49	5.37
Aug'00	14.21	9.66	4.13
Sep'00	20.66	**27.93**	7.34
Oct'00	18.77	23.14	10.63
Nov'00	**22.76**	16.57	8.21
Dec'00	18.26	16.59	6.52
Mean	15.02	14.50	6.28

Table A.51 : Monthly variation of Biopolymeric carbon (mg/g) in surface sediments
(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3
Apr'99	32.52	9.42	10.98
June'99	16.95	16.38	23.13
Aug'99	21.17	15.70	11.11
Oct'99	16.58	**37.43**	*8.98*
Dec'99	**37.68**	24.09	14.15
Jan'00	35.46	*5.95*	18.09
Feb'00	35.28	31.89	31.24
Mar'00	28.82	12.68	11.02
Apr'00	14.19	15.04	**36.23**
May'00	18.93	18.99	31.15
July'00	*11.57*	14.40	24.63
Aug'00	14.24	10.09	28.17
Sep'00	19.61	18.28	23.10
Oct'00	22.06	18.95	23.26
Nov'00	23.34	15.86	25.71
Dec'00	21.60	16.75	20.90
Mean	23.13	17.62	21.37

Table A.52 : Monthly variation of Biopolymeric carbon percentage of organic carbon in surface sediments

Month	Station 1	Station 2	Station 3
Apr'99	67.48	90.58	89.02
June'99	83.05	83.62	76.87
Aug'99	78.83	84.30	88.89
Oct'99	83.42	*62.57*	**91.02**
Dec'99	*62.32*	75.91	85.85
Jan'00	64.54	**94.05**	81.91
Feb'00	64.72	68.11	68.76
Mar'00	71.18	87.32	88.98
Apr'00	85.81	84.96	*63.77*
May'00	81.07	81.01	68.85
July'00	**88.43**	85.60	75.37
Aug'00	85.76	89.91	71.83
Sep'00	80.39	81.72	76.90
Oct'00	77.94	81.05	76.74
Nov'00	76.66	84.14	74.29
Dec'00	78.40	83.25	79.10
Mean	76.87	82.38	78.63

Table A.53 : Monthly variation of Complex organic carbon percentage of organic carbon in surface sediments

(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3
Apr'99	1.45	0.77	**5.23**
June'99	0.84	1.13	3.63
Aug'99	2.40	1.66	2.79
Oct'99	1.58	**2.24**	1.52
Dec'99	**3.01**	1.42	3.15
Jan'00	*0.07*	0.27	0.94
Feb'00	2.01	1.07	2.94
Mar'00	0.19	*0.14*	0.28
Apr'00	0.59	0.54	0.52
May'00	0.43	0.37	*0.17*
July'00	0.44	0.70	0.31
Aug'00	0.43	0.37	0.55
Sep'00	0.26	0.63	0.26
Oct'00	0.60	0.61	0.50
Nov'00	0.36	0.44	0.30
Dec'00	0.55	0.60	0.55
Mean	0.95	0.81	1.48

Table A.54:- Monthly variation of Protein:Carbohydrate ratio in surface sediments

Month	Station 1	Station 2	Station 3
Apr'99			
June'99			
Aug'99	1.642	2.671	0.831
Oct'99	1.790	3.028	0.353
Dec'99	7.101	7.920	1.554
Jan'00	7.832	7.692	1.544
Feb'00	4.041	9.585	1.299
Mar'00	**8.224**	**10.247**	1.469
Apr'00	3.427	4.259	1.267
May'00	2.041	1.606	0.853
July'00	3.314	4.092	0.961
Aug'00	*0.633*	*0.474*	**15.137**
Sep'00	0.770	1.099	0.260
Oct'00	0.733	0.848	*0.225*
Nov'00	1.413	1.592	0.334
Dec'00			
Mean	3.305	4.239	2.007

Table A.55:- Monthly variation of sedimentary sodium(mg/g)
(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3
Apr'99			
June'99			
Aug'99	2.451	2.549	0.892
Oct'99	2.847	2.693	0.486
Dec'99	3.447	3.468	0.830
Jan'00	3.298	2.854	0.755
Feb'00	2.765	3.346	0.603
Mar'00	3.404	3.369	0.612
Apr'00	2.742	2.531	0.903
May'00	0.402	0.571	0.202
July'00	**4.562**	**4.901**	**1.580**
Aug'00	0.343	*0.363*	*0.121*
Sep'00	0.605	0.637	0.188
Oct'00	0.643	0.633	0.249
Nov'00	0.610	0.701	0.211
Dec'00	*0.092*	0.654	0.587
Mean	2.015	2.091	0.587

Table A.56 :- Monthly variation of sedimentary potassium(mg/g)

Month	Station 1	Station 2	Station 3
Apr'99			
June'99			
Aug'99	0.046	0.087	**0.092**
Oct'99	0.053	0.041	0.032
Dec'99	0.030	0.051	0.033
Jan'00	0.030	0.112	0.026
Feb'00	0.051	0.076	*0.010*
Mar'00	*0.015*	*0.037*	0.044
Apr'00			
May'00	0.379	0.483	0.058
July'00			
Aug'00			
Sep'00			
Oct'00			
Nov'00			
Dec'00	**0.459**	**2.654**	0.096
Mean	0.133	0.443	0.049

Table A.57 :- Monthly variation of sedimentary calcium(mg/g)
(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3
Apr'99	5.644	6.402	1.788
June'99	9.813	11.927	4.723
Aug'99	5.845	11.532	4.056
Oct'99	**15.025**	6.638	**5.025**
Dec'99	3.987	**14.977**	1.421
Jan'00	10.111	11.319	1.339
Feb'00	7.310	8.313	1.994
Mar'00	6.651	7.734	2.008
Apr'00	6.790	7.869	2.896
May'00	0.014	0.016	0.007
July'00	13.454	14.296	5.013
Aug'00	*0.007*	*0.006*	*0.001*
Sep'00	0.014	0.016	0.005
Oct'00	0.014	0.017	0.007
Nov'00	0.014	0.019	0.007
Dec'00	0.015	0.014	0.004
Mean	5.294	6.318	1.893

Table A.58 :- Monthly variation of sedimentary magnesium(mg/g)

Month	Station 1	Station 2	Station 3
Apr'99	9418.4	8426.4	3725.5
June'99	29609.0	29806.5	9357.0
Aug'99	12496.8	23429.2	7232.2
Oct'99	22790.6	10406.3	5791.6
Dec'99	6425.8	31438.7	1898.0
Jan'00	25876.4	19350.3	1183.7
Feb'00	25675.0	21079.0	6051.3
Mar'00	23675.5	16763.9	5366.1
Apr'00	21748.8	22138.1	9600.7
May'00	37.8	37.2	20.5
July'00	**37025.1**	**34390.5**	**14979.1**
Aug'00	*12.0*	*18.7*	*4.0*
Sep'00	19.8	46.2	21.4
Oct'00	35.6	46.8	31.0
Nov'00	30.0	53.7	41.0
Dec'00	47.5	27.8	22.0
Mean	13432.8	13591.2	4082.8

Table A.59:- Monthly variation of sedimentary iron(µg/g)
(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3
Apr'99	38.43	*21.84*	0.90
June'99	76.60	104.31	25.26
Aug'99	53.45	77.58	32.45
Oct'99	56.22	84.05	7.93
Dec'99	*18.51*	117.10	*0.00*
Jan'00	65.16	75.13	*0.00*
Feb'00	60.25	35.97	15.34
Mar'00	39.89	41.59	13.09
Apr'00	64.72	87.48	26.31
May'00	204.00	173.40	101.31
July'00	144.37	68.29	40.90
Aug'00	49.38	*31.63*	8.72
Sep'00	148.64	203.65	87.42
Oct'00	**217.68**	**205.35**	**125.04**
Nov'00	195.63	196.50	108.67
Dec'00	175.93	110.16	63.52
Mean	100.55	102.13	41.05

Table A.60 :- Monthly variation of sedimentary chromium (µg/g)

Month	Station 1	Station 2	Station 3
Apr'99	18.87	35.50	18.48
June'99	85.73	106.30	32.39
Aug'99	25.47	62.94	22.38
Oct'99	62.57	*34.61*	32.97
Dec'99	*9.08*	129.70	5.10
Jan'00	74.27	77.72	*0.00*
Feb'00	46.70	61.93	16.29
Mar'00	45.03	47.21	21.88
Apr'00	56.17	89.88	29.11
May'00	141.73	168.55	81.68
July'00	148.27	107.29	45.83
Aug'00	87.54	74.31	25.84
Sep'00	**181.75**	**223.02**	64.03
Oct'00	161.85	196.61	**108.29**
Nov'00	158.16	204.75	92.63
Dec'00	57.50	63.99	46.37
Mean	85.04	105.27	40.20

Table A.61 :- Monthly variation of sedimentary manganese(µg/g)
(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3
Apr'99	47.69	*18.55*	4.19
June'99	72.24	71.60	15.55
Aug'99	*13.99*	46.35	4.40
Oct'99	52.31	37.31	13.40
Dec'99	20.29	86.40	*0.00*
Jan'00	62.78	50.42	*0.00*
Feb'00	33.68	26.77	6.44
Mar'00	28.46	30.00	5.92
Apr'00	34.91	46.62	19.28
May'00	232.53	214.01	134.37
July'00	87.95	92.19	9.21
Aug'00	44.61	50.00	13.58
Sep'00	262.40	**317.76**	103.46
Oct'00	250.79	258.22	79.18
Nov'00	**266.40**	282.14	**173.59**
Dec'00	225.14	182.40	107.42
Mean	108.51	113.17	43.12

Table A.62:- Monthly variation of sedimentary nickel(µg/g)

Month	Station 1	Station 2	Station 3
Apr'99	34.65	18.25	6.29
June'99	44.45	50.46	17.56
Aug'99	38.46	60.50	13.49
Oct'99	50.84	63.38	13.93
Dec'99	19.76	61.60	*2.93*
Jan'00	55.85	30.89	7.60
Feb'00	18.01	*12.69*	5.16
Mar'00	*14.26*	15.11	5.03
Apr'00	20.77	24.61	15.42
May'00	65.59	52.01	28.28
July'00	48.49	46.89	15.27
Aug'00	16.22	17.45	4.08
Sep'00	**69.69**	**110.03**	**78.63**
Oct'00	62.14	55.03	32.28
Nov'00	67.17	64.15	49.72
Dec'00	38.21	36.00	23.77
Mean	41.54	44.94	19.97

Table A.63:- Monthly variation of sedimentary copper(µg/g)
(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3
Apr'99	100.36	50.86	23.87
June'99	141.30	168.93	46.50
Aug'99	132.37	224.43	46.52
Oct'99	293.31	177.09	73.34
Dec'99	47.70	180.67	*11.04*
Jan'00	140.82	100.84	*11.06*
Feb'00	54.77	45.59	14.80
Mar'00	48.52	51.65	13.25
Apr'00	61.44	89.23	37.16
May'00	125.02	847.36	77.35
July'00	161.60	201.20	55.17
Aug'00	53.14	*43.56*	19.26
Sep'00	154.31	378.00	80.16
Oct'00	128.04	137.31	**196.03**
Nov'00	**655.88**	**940.46**	95.65
Dec'00	*39.61*	91.68	21.87
Mean	146.14	233.05	51.44

Table A.64 :- Monthly variation of sedimentary zinc (µg/g)

Month	Station 1	Station 2	Station 3
Apr'99	*0*	4.99	2.00
June'99	27.78	15.96	4.81
Aug'99	19.98	*0.00*	0.98
Oct'99	14.67	8.99	7.05
Dec'99	*0.00*	47.23	*0.00*
Jan'00	17.83	15.94	*0.00*
Feb'00	15.43	14.44	3.49
Mar'00	16.47	13.95	*2.35*
Apr'00	21.77	21.18	5.03
May'00	57.25	14.67	43.84
July'00	34.92	24.75	7.84
Aug'00	19.45	17.55	5.92
Sep'00	**126.60**	**113.70**	38.67
Oct'00	39.55	46.14	25.21
Nov'00	45.41	53.78	**72.66**
Dec'00	51.18	36.07	15.48
Mean	31.77	28.08	14.71

Table A.65 :- Monthly variation of sedimentary lead (µg/g)
(Maximum in Bold, Minimum in Italics and underlined)

Month	Station 1	Station 2	Station 3
Apr'99	30.88	21.94	16.98
June'99	45.64	45.87	15.23
Aug'99	44.96	**63.43**	9.77
Oct'99	**73.33**	49.44	26.45
Dec'99	19.58	59.04	7.53
Jan'00	51.50	41.85	13.82
Feb'00	15.67	16.46	*5.81*
Mar'00	*14.32*	*13.30*	6.00
Apr'00	15.24	20.67	9.63
May'00	40.06	42.64	35.21
July'00	41.90	35.63	15.31
Aug'00	19.79	28.25	22.92
Sep'00	59.74	56.10	28.91
Oct'00	47.24	46.32	36.01
Nov'00	54.56	54.55	**39.81**
Dec'00	24.33	19.53	11.35
Mean	37.42	38.44	18.80

Table A.66 :- Monthly variation of sedimentary cobalt (µg/g)
(Maximum in Bold, Minimum in Italics and underlined)

Appendix B

ANOVA

Source of Variation	DF	SS	MS	F	P	Fcrit
Temperature						
Season	2	12.634	6.317	14.494	0.005	5.14
Station	3	7.314	2.438	5.594	0.036	4.76
Residual	6	2.615	0.436			
Total	11	22.563	2.051			
pH						
Season	2	0.163	0.0814	1.172	0.372	5.14
Station	3	0.360	0.120	1.729	0.260	4.76
Residual	6	0.417	0.0695			
Total	11	0.940	0.0855			
Salinity						
Season	2	385.460	192.730	67.126	<0.001	5.14
Station	3	145.200	48.400	16.857	0.003	4.76
Residual	6	17.227	2.871			
Total	11	547.887	49.808			
DO						
Season	2	4.265	2.132	1.412	0.314	5.14
Station	3	3.534	1.178	0.780	0.547	4.76
Residual	6	9.064	1.511			
Total	11	16.862	1.533			
Alkalinity						
Season	2	0.909	0.455	10.628	0.011	5.14
Station	3	1.070	0.357	8.341	0.015	4.76
Residual	6	0.257	0.0428			
Total	11	2.236	0.203			
Hardness						
Season	2	23.132	11.566	49.603	<0.001	5.14
Station	3	3.426	1.142	4.898	0.047	4.76
Residual	6	1.399	0.233			
Total	11	27.957	2.542			
TSS						
Season	2	2855.124	1427.562	2.876	0.133	5.14
Station	3	2786.506	928.835	1.871	0.235	4.76
Residual	6	2978.663	496.444			
Total	11	8620.293	783.663			

Table B.1:- Two way-ANOVA showing significant difference between stations and seasons for hydrographical parameters.

Source of Variation	DF	SS	MS	F	P	Fcrit
Temperature						
Station	2	1.407	0.704	0.585	0.569	3.63
Time	8	31.185	3.898	3.238	0.022	2.59
Residual	16	19.259	1.204			
Total	26	51.852	1.994			
pH						
Station	2	0.576	0.288	2.376	0.125	3.63
Time	8	0.453	0.0567	0.468	0.861	2.59
Residual	16	1.938	0.121			
Total	26	2.967	0.114			
Salinity						
Station	2	268.292	134.146	27.855	<0.001	3.63
Time	8	42.097	5.262	1.093	0.416	2.59
Residual	16	77.055	4.816			
Total	26	387.444	14.902			
Dissolved Oxygen						
Station	2	10.526	5.263	2.865	0.086	3.63
Time	8	38.507	4.813	2.620	0.048	2.59
Residual	16	29.397	1.837			
Total	26	78.431	3.017			
Alkalinity						
Station	2	2.285	1.143	1.563	0.240	3.63
Time	8	4.736	0.592	0.810	0.604	2.59
Residual	16	11.698	0.731			
Total	26	18.719	0.720			
Chlorophyll						
Station	2	256.178	128.089	72.933	<0.001	3.63
Time	8	13.499	1.687	0.961	0.498	2.59
Residual	16	28.100	1.756			
Total	26	297.777	11.453			
Total Suspended Solids						
Station	2	135.924	67.962	0.183	0.834	3.63
Time	8	3996.608	499.576	1.346	0.291	2.59
Residual	16	5940.615	371.288			
Total	26	10073.15	387.429			

Table B.2:- Two way-ANOVA showing significant spatial and diurnal variation for hydrographical parameters.

Source of Variation	DF	SS	MS	F	P	Fcrit
Dissolved Total Amino acids						
Season	2	30.120	15.060	0.121	0.888	5.14
Station	3	380.541	126.847	1.017	0.448	4.76
Residual	6	748.524	124.754			
Total	11	1159.19	105.380			
Dissolved Combined Amino acids						
Season	2	32.152	16.076	0.126	0.884	5.14
Station	3	387.534	129.178	1.010	0.451	4.76
Residual	6	767.216	127.869			
Total	11	1186.9	107.900			
Dissolved Free Amino acids						
Season	2	0.0546	0.0273	0.343	0.723	5.14
Station	3	0.203	0.0677	0.851	0.515	4.76
Residual	6	0.478	0.0796			
Total	11	0.735	0.0669			
Dissolved Proteins						
Season	2	178.35	89.175	7.287	0.025	5.14
Station	3	36.969	12.323	1.007	0.452	4.76
Residual	6	73.427	12.238			
Total	11	288.745	26.250			
Dissolved Monosaccharides						
Season	2	5.697	2.848	0.336	0.727	5.14
Station	3	9.382	3.127	0.369	0.778	4.76
Residual	6	50.792	8.465			
Total	11	65.871	5.988			
Dissolved Polysaccharides						
Season	2	600.57	300.287	4.251	0.071	5.14
Station	3	44.617	14.872	0.211	0.886	4.76
Residual	6	423.827	70.638			
Total	11	1069.02	97.183			
Dissolved Total Lipids						
Season	2	0.582	0.291	2.072	0.207	5.14
Station	3	0.498	0.166	1.181	0.393	4.76
Residual	6	0.843	0.141			
Total	11	1.923	0.175			
Dissolved Tannin and Lignin						
Season	2	0.0013	0.00066	0.0136	0.987	5.14
Station	3	1.843	0.614	12.682	0.005	4.76
Residual	6	0.291	0.0484			
Total	11	2.135	0.194			
Dissolved Humic Substances						
Season	2	20.147	10.073	9.091	0.015	5.14
Station	3	146.85	48.951	44.178	<0.001	4.76
Residual	6	6.648	1.108			
Total	11	173.65	15.786			

Table B.3:- Results of ANOVA showing significant variation between stations and seasons for dissolved organic constituents.

Source of Variation	DF	SS	MS	F	P	Fcrit
Dissolved Proteins						
Station	2	90.192	45.096	1.740	0.207	3.63
Time	8	662.952	82.869	3.198	0.023	2.59
Residual	16	414.666	25.917			
Total	26	1167.811	44.916			
Dissolved Monosaccharides						
Station	2	7.325	3.663	3.214	0.067	3.63
Time	8	118.094	14.762	12.956	<0.001	2.59
Residual	16	18.231	1.139			
Total	26	143.650	5.525			
Dissolved Polysaccharides						
Station	2	68.457	34.228	1.414	0.272	3.63
Time	8	358.212	44.776	1.850	0.140	2.59
Residual	16	387.358	24.210			
Total	26	814.027	31.309			
Dissolved Lipids						
Station	2	0.0662	0.0331	0.365	0.699	3.63
Time	8	2.354	0.294	3.248	0.021	2.59
Residual	16	1.450	0.0906			
Total	26	3.870	0.149			
Dissolved Tannin and Lignin						
Station	2	7.817	3.908	4.907	0.022	3.63
Time	8	17.594	2.199	2.761	0.040	2.59
Residual	16	12.744	0.797			
Total	26	38.155	1.468			

Table B.4:- Results of ANOVA showing significant spatial and diurnal variation of dissolved organic constituents

Source of Variation	DF	SS	MS	F	P	Fcrit
Particulate Total Aminoacids						
Season	2	0.275	0.137	2.123	0.201	5.14
Station	3	1.821	0.607	9.391	0.011	4.76
Residual	6	0.388	0.0646			
Total	11	2.484	0.226			
Particulate Free Aminoacids						
Season	2	0.0630	0.0315	2.410	0.171	5.14
Station	3	0.0934	0.0311	2.379	0.169	4.76

Residual	6	0.0785	0.0131			
Total	11	0.235	0.0214			
Particulate Combined Aminoacids						
Season	2	0.168	0.0842	1.290	0.342	5.14
Station	3	0.918	0.306	4.687	0.052	4.76
Residual	6	0.392	0.0653			
Total	11	1.479	0.134			
Particulate Proteins						
Season	2	0.577	0.288	1.044	0.408	5.14
Station	3	1.632	0.544	1.970	0.220	4.76
Residual	6	1.657	0.276			
Total	11	3.865	0.351			
Particulate Total Carbohydrates						
Season	2	1.067	0.534	2.377	0.174	5.14
Station	3	1.841	0.614	2.734	0.136	4.76
Residual	6	1.347	0.224			
Total	11	4.255	0.387			
Particulate Monosaccharides						
Season	2	0.525	0.262	8.674	0.017	5.14
Station	3	0.226	0.075	2.491	0.157	4.76
Residual	6	0.182	.0303			
Total	11	0.932	0.0848			
Particulate Polysaccharides						
Season	2	0.190	0.0949	0.535	0.611	5.14
Station	3	0.911	0.304	1.712	0.263	4.76
Residual	6	1.064	0.177			
Total	11	2.165	0.197			
Particulate Total Lipids						
Season	2	57.698	28.849	1.820	0.241	5.14
Station	3	73.069	24.356	1.537	0.299	4.76
Residual	6	95.094	15.849			
Total	11	225.861	20.533			
Particulate Tannin and Lignin						
Season	2	0.0994	0.0497	0.783	0.499	5.14
Station	3	0.334	0.111	1.753	0.256	4.76
Residual	6	0.381	0.0635			
Total	11	0.814	0.0740			
Particulate Humic Substances						
Season	2	1.263	0.631	0.830	0.480	5.14
Station	3	3.045	1.015	1.335	0.348	4.76
Residual	6	4.563	0.760			
Total	11	8.871	0.806			

Table B.5:- Results of Two-way ANOVA showing significant difference between stations and seasons in particulate organic matter.

Source of Variation	DF	SS	MS	F	P	Fcrit
Particulate Organic Carbon						
Station	2	30.742	15.371	10.162	0.006	4.46
Time	4	9.374	2.344	1.549	0.277	3.84
Residual	8	12.101	1.513			
Total	14	52.217	3.730			
Particulate Free Aminoacids						
Station	2	0.0276	0.0138	2.862	0.115	4.46
Time	4	0.0164	0.0041	0.849	0.533	3.84
Residual	8	0.0386	0.00482			
Total	14	0.0826	0.00590			
Particulate Proteins						
Station	2	0.0449	0.0224	3.587	0.077	4.46
Time	4	0.0279	0.007	1.116	0.413	3.84
Residual	8	0.0500	0.00625			
Total	14	0.123	0.00877			
Particulate Total Carbohydrates						
Station	2	0.902	0.451	40.875	<0.001	4.46
Time	4	0.106	0.0266	2.413	0.135	3.84
Residual	8	0.0882	0.0110			
Total	14	1.096	0.0783			
Particulate Monosaccharides						
Station	2	0.486	0.243	10.598	0.006	4.46
Time	4	0.0765	0.0191	0.833	0.540	3.84
Residual	8	0.184	0.0229			
Total	14	0.746	0.0533			
Particulate Polysaccharides						
Station	2	0.173	0.0863	2.618	0.133	4.46
Time	4	0.149	0.0373	1.132	0.407	3.84
Residual	8	0.264	0.0330			
Total	14	0.585	0.0418			
Particulate Total Lipids						
Station	2	1.545	0.772	4.660	0.046	4.46
Time	4	1.909	0.477	2.881	0.095	3.84
Residual	1.326	0.166				
Total	14	4.780	0.341			
Particulate Tannin and Lignin						
Station	2	3.721	1.861	2.389	0.154	4.46
Time	4	25.057	6.264	8.044	0.007	3.84
Residual	8	6.230	0.779			
Total	14	35.009	2.501			
Particulate Humic Substances						
Station	2	1.210	0.605	2.916	0.112	4.46
Time	4	1.195	0.299	1.439	0.306	3.84
Residual	8	1.661	0.208			
Total	14	4.066	0.290			

Table B.6:- Results of Two-way ANOVA showing significant difference between stations and time in particulate organic matter.

Source of Variation	DF	SS	MS	F	P	Fcrit
Sedimentary Organic Carbon						
Season	2	1045.5	522.75	9.060	0.015	6.94
Station	3	7964.95	2654.982	46.014	<0.001	6.94
Residual	6	346.198	57.700			
Total	11	9356.65	850.604			
Sedimentary Organic Nitrogen						
Season	2	13.128	6.564	0.794	0.494	6.94
Station	3	19.461	6.487	0.785	0.545	6.94
Residual	6	49.599	8.266			
Total	11	82.188	7.472			
Sedimentary Total Aminoacids						
Season	2	22.520	11.260	2.094	0.204	6.94
Station	3	122.5	40.834	7.593	0.018	6.94
Residual	6	32.267	5.378			
Total	11	177.29	16.117			
Sedimentary Free Aminoacids						
Season	2	0.0146	0.00730	6.028	0.037	6.94
Station	3	0.118	0.0393	32.411	<0.001	6.94
Residual	6	0.0073	0.00121			
Total	11	0.140	0.0127			
Sedimentary Combined Aminoacids						
Season	2	21.452	10.726	1.992	0.217	6.94
Station	3	115.48	38.492	7.147	0.021	6.94
Residual	6	32.313	5.385			
Total	11	169.24	15.386			
Sedimentary Proteins						
Season	2	13.079	6.540	2.266	0.185	6.94
Station	3	77.468	25.823	8.949	0.012	6.94
Residual	6	17.313	2.886			
Total	11	107.86	9.805			
Sedimentary Monosaccharides						
Season	2	0.045	0.0225	2.182	0.194	6.94
Station	3	0.998	0.333	32.261	<0.001	6.94
Residual	6	0.0619	0.0103			
Total	11	1.105	0.100			
Sedimentary Total Carbohydrates						
Season	2	51.854	25.927	10.858	0.010	6.94
Station	3	341.07	113.691	47.614	<0.001	6.94
Residual	6	14.326	2.388			
Total	11	407.25	37.023			
Sedimentary Polysaccharides						
Season	2	49.239	24.620	10.992	0.010	6.94

Station	3	325.85	108.617	48.495	<0.001	6.94
Residual	6	13.438	2.240			
Total	11	388.53	35.321			
Sedimentary Total Lipids						
Season	2	0.262	0.131	0.225	0.805	6.94
Station	3	15.498	5.166	8.860	0.013	6.94
Residual	6	3.499	0.583			
Total	11	19.259	1.751			
Sedimentary Tannin and Lignin						
Season	2	0.311	0.156	0.474	0.644	6.94
Station	3	21.479	7.160	21.793	0.001	6.94
Residual	6	1.971	0.329			
Total	11	23.761	2.160			
Sedimentary Humic Substances						
Season	2	9.372	4.686	1.287	0.343	6.94
Station	3	171.34	57.112	15.680	0.003	6.94
Residual	6	21.853	3.642			
Total	11	202.561	18.415			

Table B.7:- Two way-ANOVA showing significance variation between seasons and stations for various organic constituents in surface sediments.

Source of Variation	DF	SS	MS	F	P	Fcrit
SOC						
Station	2	29107.7	14553.823	551.75	<0.001	3.635
Season	2	1823.73	911.862	34.569	<0.001	3.635
Depth	4	2329.5	582.386	22.079	<0.001	3.01
Residual	16	422.044	26.378			
Total	44	36374.8	826.700			
SON						
Station	2	75.807	37.904	689.192	<0.001	3.635
Season	2	1.541	0.771	14.014	<0.001	3.635
Depth	5	14.607	2.921	53.119	<0.001	3.01
Residual	20	1.100	0.0550			
Total	53	103.58	1.954			
C/N						
Station	2	322.03	161.016	17.156	<0.001	3.635
Season	2	218.63	109.317	11.648	<0.001	3.635
Depth	5	192.83	38.566	4.109	0.010	3.01
Residual	20	187.71	9.385			
Total	53	1249.35	23.573			
STAA						
Station	2	348.23	174.113	39.243	<0.001	3.635
Season	2	89.877	44.939	10.129	<0.001	3.635
Depth	5	97.027	19.405	4.374	0.007	3.01
Residual	20	88.736	4.437			
Total	53	742.95	14.018			

SFAA						
Station	2	5.662	2.831	3.510	0.054	3.635
Season	2	4.291	2.146	2.660	0.101	3.635
Depth	4	3.111	0.778	0.964	0.454	3.01
Residual	16	12.905	0.807			
Total	44	47.375	1.077			
SCAA						
Station	2	274.92	137.458	31.570	<0.001	3.635
Season	2	84.494	42.247	9.703	0.002	3.635
Depth	4	69.853	17.463	4.011	0.019	3.01
Residual	16	69.666	4.354			
Total	44	606.686	13.788			
SP						
Station	2	108.04	54.017	66.092	<0.001	3.635
Season	2	71.075	35.538	43.481	<0.001	3.635
Depth	4	34.113	8.528	10.435	<0.001	3.01
Residual	16	13.077	0.817			
Total	44	259.77	5.904			

Table B.8a:- Three way-ANOVA showing significance variation between seasons and stations for various organic constituents in core sediments

Source of Variation	DF	SS	MS	F	P	Fcrit
SMCHO						
Station	2	1.719	0.859	24.226	<0.001	3.635
Season	2	0.936	0.468	13.200	<0.001	3.635
Depth	4	0.421	0.105	2.967	0.052	3.01
Residual	16	0.568	0.0355			
Total	44	5.661	0.129			
STCHO						
Station	2	1118.2	559.122	95.579	<0.001	3.635
Season	2	106.562	53.281	9.108	0.002	3.635
Depth	4	162.465	40.616	6.943	0.002	3.01
Residual	16	93.598	5.850			
Total	44	1637.1	37.206			
SPCHO						
Station	2	962.6	481.302	81.115	<0.001	3.635
Season	2	76.266	38.133	6.427	0.009	3.635
Depth	4	175.66	43.915	7.401	0.001	3.01
Residual	16	94.937	5.934			
Total	44	1486.5	33.784			
ST&L						
Station	2	33.227	16.614	79.653	<0.001	3.635
Season	2	7.526	3.763	18.041	<0.001	3.635
Depth	4	14.821	3.705	17.764	<0.001	3.01
Residual	16	3.337	0.209			
Total	44	64.459	1.465			

STL						
Station	2	24.643	12.322	48.132	<0.001	3.635
Season	2	20.964	10.482	40.945	<0.001	3.635
Depth	4	4.072	1.018	3.977	0.020	3.01
Residual	16	4.096	0.256			
Total	44	63.491	1.443			
SHS						
Station	2	1608.9	804.450	213.68	<0.001	3.635
Season	2	548.84	274.420	72.891	<0.001	3.635
Depth	4	237.50	59.376	15.771	<0.001	3.01
Residual	16	60.237	3.765			
Total	44	2722.3	61.870			

Table B.8b:- Three way-ANOVA showing significance variation between seasons and stations for various organic constituents in core sediments

Source of Variation	DF	SS	MS	F	P	Fcrit
STAA/SOC						
Season	2	13.101	6.550	0.334	0.735	6.94
Station	2	97.692	48.846	2.487	0.199	6.94
Residual	4	78.558	19.640			
Total	8	189.351	23.669			
SFAA/SOC						
Season	2	0.000357	0.000179	0.141	0.873	6.94
Station	2	0.00594	0.00297	2.341	0.212	6.94
Residual	4	0.00507	0.00127			
Total	8	0.0114	0.00142			
SCAA/SOC						
Season	2	12.971	6.486	0.330	0.737	6.94
Station	2	97.183	48.592	2.473	0.200	6.94
Residual	4	78.609	19.652			
Total	8	188.764	23.595			
SMCHO/SOC						
Season	2	0.141	0.0703	2.670	0.183	6.94
Station	2	0.0814	0.0407	1.545	0.318	6.94
Residual	4	0.105	0.0263			
Total	8	0.327	0.0409			
STCHO/SOC						
Season	2	9.344	4.672	0.814	0.505	6.94
Station	2	24.317	12.159	2.118	0.236	6.94
Residual	4	22.964	5.741			
Total	8	56.625	7.078			
SPCHO/SOC						
Season	2	7.218	3.609	0.647	0.571	6.94
Station	2	24.504	12.252	2.197	0.227	6.94
Residual	4	22.306	5.576			
Total	8	54.029	6.754			

SP/SOC						
Season	2	5.122	2.561	0.737	0.534	6.94
Station	2	4.347	2.173	0.626	0.580	6.94
Residual	4	13.895	3.474			
Total	8	23.364	2.920			
STL/SOC						
Season	2	1.905	0.953	3.438	0.135	6.94
Station	2	1.365	0.682	2.463	0.201	6.94
Residual	4	1.108	0.277			
Total	8	4.378	0.547			

Table B.9a:- Two way-ANOVA showing significance variation between seasons and stations for various parameters in surface sediments.

Source of Variation	DF	SS	MS	F	P	Fcrit
SPBC						
Season	2	20.047	10.023	5.380	0.073	6.94
Station	2	139.962	69.9813	7.564	0.003	6.94
Residual	4	7.452	1.863			
Total	8	167.461	20.933			
SBPC/SOC						
Season	2	35.672	17.836	1.421	0.342	6.94
Station	2	48.353	24.176	1.926	0.260	6.94
Residual	4	50.212	12.553			
Total	8	134.238	16.780			
COC/SOC						
Season	2	35.672	17.836	1.421	0.342	6.94
Station	2	48.353	24.176	1.926	0.260	6.94
Residual	4	50.212	12.553			
Total	8	134.238	16.780			
SP/STCHO						
Season	2	0.00862	0.00431	0.0567	0.946	6.94
Station	2	0.815	0.407	5.355	0.074	6.94
Residual	4	0.304	0.0761			
Total	8	1.128	0.141			
C/N						
Season	2	38.315	19.157	0.912	0.472	6.94
Station	2	9.213	4.607	0.219	0.812	6.94
Residual	4	84.044	21.011			
Total	8	131.572	16.446			
STCHO/SPBC						
Season	2	1.572	0.786	0.0414	0.960	6.94
Station	2	27.000	13.500	0.711	0.544	6.94
Residual	4	75.999	19.000			
Total	8	104.571	13.071			
SP/SPBC						
Season	2	13.727	6.863	0.866	0.487	6.94

Station	2	60.585	30.292	3.823	0.118	6.94
Residual	4	31.695	7.924			
Total	8	106.006	13.251			
STL/SPBC						
Season	2	24.521	12.261	0.619	0.583	6.94
Station	2	23.099	11.550	0.583	0.599	6.94
Residual	4	79.209	19.802			
Total	8	126.830	15.854			

Table B.9b:- Two way-ANOVA showing significance variation between seasons and stations for various organic constituents in surface sediments.

Source of Variation	DF	SS	MS	F	P	Fcrit
SP/SON						
Season	2	32.677	16.338	0.541	0.619	6.94
Station	2	592.201	296.100	9.813	0.029	6.94
Residual	4	120.693	30.173			
Total	8	745.570	93.196			
STAA/SON						
Season	2	523.618	261.809	17.884	0.010	6.94
Station	2	1314.122	657.061	44.885	0.002	6.94
Residual	4	58.556	14.639			
Total	8	1896.296	237.037			
SFAA/SON						
Season	2	0.344	0.172	1.279	0.372	6.94
Station	2	0.0139	0.00693	0.0516	0.950	6.94
Residual	4	0.538	0.134			
Total	8	0.896	0.112			
SCAA/SON						
Season	2	497.436	248.718	20.431	0.008	6.94
Station	2	1310.724	655.362	53.835	0 001	6.94
Residual	4	48.694	12.174			
Total	8	1856.854	232.107			

Table B.9c:- Two way-ANOVA showing significance variation between seasons and stations for various organic constituents (as percentage of organic nitrogen) in surface sediments.

Source of Variation	DF	SS	MS	F	P	Fcrit
(STAA-C/SOC)%						
Station	2	160.3	80.144	12.5	<0.001	3.635
Season	2	129.37	64.682	10.087	<0.001	3.635
Depth	5	7.030	1.406	0.219	0.950	3.01
Residual	20	128.25	6.413			
Total	53	520.84	9.827			
(SFAA-C/SOC)%						
Station	2	0.881	0.440	2.188	0.138	3.635
Season	2	0.662	0.331	1.644	0.218	3.635

Depth	5	1.454	0.291	1.445	0.251	3.01
Residual	20	4.024	0.201			
Total	53	12.321	0.232			
(SCAA-C/SOC)%						
Station	2	97.168	48.584	8.946	0.002	3.635
Season	2	85.593	42.796	7.880	0.003	3.635
Depth	5	7.850	1.570	0.289	0.913	3.01
Residual	20	108.62	5.431			
Total	53	413.94	7.810			
(SMCHO-C/SOC)%						
Station	2	0.914	0.457	3.622	0.045	3.635
Season	2	1.465	0.733	5.808	0.010	3.635
Depth	5	0.892	0.178	1.415	0.262	3.01
Residual	20	2.522	0.126			
Total	53	10.166	0.192			
(STCHO-C/SOC)%						
Station	2	607.1	303.530	124.793	<0.001	3.635
Season	2	16.17	8.085	3.324	0.057	3.635
Depth	5	44.639	8.928	3.671	0.016	3.01
Residual	20	48.645	2.432			
Total	53	938.071	17.699			
(SPCHO-C/SOC)%						
Station	2	591.29	295.644	88.589	<0.001	3.635
Season	2	7.249	3.625	1.086	0.357	3.635
Depth	5	42.446	8.489	2.544	0.061	3.01
Residual	20	66.745	3.337			
Total	53	927.13	17.493			
(SP-C/SOC)%						
Station	2	31.041	15.521	26.829	<0.001	3.635
Season	2	53.974	26.987	46.649	<0.001	3.635
Depth	5	3.382	0.676	1.169	0.359	3.01
Residual	20	11.570	0.579			
Total	53	128.421	2.423			
(STL-C/SOC)%						
Station	2	10.734	5.367	12.308	<0.001	3.635
Season	2	26.922	13.461	30.870	<0.001	3.635
Depth	5	0.455	0.0911	0.209	0.955	3.01
Residual	20	8.721	0.436			
Total	53	59.338	1.120			

Table B.10a:- Three way-ANOVA showing significance variation between stations seasons and depth for various organic constituents (as percentage of organic carbon) in core sediments

Source of Variation	DF	SS	MS	F	P	Fcrit
SBPC						
Station	2	582.5	291.267	147.39	<0.001	3.635
Season	2	147.6	73.776	37.331	<0.001	3.635
Depth	5	126.82	25.363	12.834	<0.001	3.01
Residual	20	39.525	1.976			
Total	53	995.64	18.786			
SBPC%						
Station	2	1129.96	564.981	137.389	<0.001	3.635
Season	2	205.54	102.769	24.991	<0.001	3.635
Depth	5	39.466	7.893	1.919	0.136	3.01
Residual	20	82.245	4.112			
Total	53	1808.76	34.127			
COC%						
Station	2	1129.96	564.981	137.39	<0.001	3.635
Season	2	205.54	102.769	24.991	<0.001	3.635
Depth	5	39.466	7.893	1.919	0.136	3.01
Residual	20	82.245	4.112			
Total	53	1808.76	34.127			
SP/STCHO						
Station	2	0.0154	0.00772	1.326	0.288	3.635
Season	2	0.290	0.145	24.914	<0.001	3.635
Depth	5	0.0698	0.0140	2.397	0.074	3.01
Residual	20	0.117	0.00583			
Total	53	0.645	0.0122			
C/N						
Station	2	322.045	161.022	17.150	<0.001	3.635
Season	2	218.680	109.340	11.646	<0.001	3.635
Depth	5	192.720	38.544	4.105	0.010	3.01
Residual	20	187.781	9.389			
Total	53	1249.43	23.574			
(STL/ SBPC)%						
Station	2	72.947	36.474	5.909	0.010	3.635
Season	2	258.78	129.390	20.964	<0.001	3.635
Depth	5	7.286	1.457	0.236	0.942	3.01
Residual	20	123.441	6.172			
Total	53	806.654	15.220			
(SP/ SBPC)%						
Station	2	28.581	14.291	0.976	0.394	3.635
Season	2	780.05	390.025	26.634	<0.001	3.635
Depth	5	186.769	37.354	2.551	0.061	3.01
Residual	20	292.883	14.644			
Total	53	1675.93	31.621			
(STCHO/ SBPC)%						
Station	2	140.39	70.197	4.563	0.023	3.635
Season	2	1052.8	526.382	34.220	<0.001	3.635
Depth	5	204.19	40.838	2.655	0.054	3.01
Residual	20	307.65	15.382			
Total	53	2215.91	41.810			

Table B.10b:- Three way-ANOVA showing significance variation between stations seasons and depth for various organic constituents in core sediments

Source of Variation	DF	SS	MS	F	P	Fcrit
(STAA/SON)%						
Station	2	9970.39	4985.194	28.863	<0.001	3.635
Season	2	556.313	278.156	1.610	0.225	3.635
Depth	5	207.627	41.525	0.240	0.940	3.01
Residual	20	3454.39	172.720			
Total	53	18696.5	52.764			
(SFAA/SON)%						
Station	2	23.038	11.519	1.630	0.221	3.635
Season	2	29.677	14.838	2.099	0.149	3.635
Depth	5	51.170	10.234	1.448	0.251	3.01
Residual	20	141.366	7.068			
Total	53	408.835	7.714			
(SCAA/SON)%						
Station	2	9871.85	4935.926	29.330	<0.001	3.635
Season	2	790.464	395.232	2.349	0.121	3.635
Depth	5	330.780	66.156	0.393	0.848	3.01
Residual	20	3365.74	168.287			
Total	53	18619.4	351.309			
SP/SON						
Station	2	5244.01	2622.006	53.657	<0.001	3.635
Season	2	2986.56	1493.280	30.559	<0.001	3.635
Depth	5	83.963	16.793	0.344	0.880	3.01
Residual	20	977.321	48.866			
Total	53	11454.4	216.121			

Table B.10c:- Three way-ANOVA showing significance variation between stations seasons and depth for various organic constituents (as percentage of organic nitrogen) in core sediments

Source of Variation	DF	SS	MS	F	P	Fcrit
Sedimentary Sodium						
Season	2	2.870	1.435	0.352	0.717	6.94
Station	3	8.064	2.688	0.660	0.606	6.94
Residual	6	24.437	4.073			
Total	11	35.371	3.216			
Sedimentary Potassium						
Season	2	0.316	0.158	8.724	0.017	6.94
Station	3	6.179	2.060	113.7	<0.001	6.94
Residual	6	0.109	0.0181			
Total	11	6.603	0.600			
Sedimentary Calcium						
Season	2	0.0573	0.0287	1.006	0.420	6.94
Station	3	0.154	0.0514	1.806	0.246	6.94
Residual	6	0.171	0.0285			
Total	11	0.382	0.0348			
Sedimentary Magnesium						
Season	2	4.471	2.236	8.131	0.020	6.94

Station	3	41.965	13.988	50.879	<0.001	6.94
Residual	6	1.650	0.275			
Total	11	48.086	4.371			

Table B.11a:- Two way-ANOVA showing significance variation between seasons and stations for major elements in surface sediments.

Source of Variation	DF	SS	MS	F	P	Fcrit
Sedimentary Iron						
Season	2	90.792	45.396	12.641	0.007	6.94
Station	3	224.94	74.980	20.879	0.001	6.94
Residual	6	21.547	3.591			
Total	11	337.28	30.662			
Sedimentary Manganese						
Season	2	0.0012	0.000608	3.085	0.120	6.94
Station	3	0.0085	0.00283	14.352	0.004	6.94
Residual	6	0.0012	0.000197			
Total	11	0.0109	0.000990			
Sedimentary Nickel						
Season	2	0.0067	0.00336	19.820	0.002	6.94
Station	3	0.0170	0.00565	33.361	<0.001	6.94
Residual	6	0.0010	0.000169			
Total	11	0.0247	0.00224			
Sedimentary Copper						
Season	2	0.0011	0.000558	9.571	0.014	6.94
Station	3	0.0014	0.000475	8.143	0.015	6.94
Residual	6	0.0004	0.000058			
Total	11	0.0029	0.000263			
Sedimentary Zinc						
Season	2	0.0078	0.00391	3.963	0.080	6.94
Station	3	0.0622	0.0207	21.037	0.001	6.94
Residual	6	0.0059	0.000986			
Total	11	0.0760	0.00691			
Sedimentary Cobalt						
Season	2	0.001	0.000475	11.400	0.009	6.94
Station	3	0.0014	0.000475	11.400	0.007	6.94
Residual	6	0.0003	0.0000417			
Total	11	0.0027	0.000239			
Sedimentary Lead						
Season	2	0.0009	0.000408	0.277	0.767	6.94
Station	3	0.0026	0.000875	0.593	0.642	6.94
Residual	6	0.0089	0.00148			
Total	11	0.0123	0.00112			
Sedimentary Chromium						
Season	2	0.0028	0.00141	16.355	0.004	6.94
Station	3	0.0108	0.00361	41.935	<0.001	6.94
Residual	6	0.0005	0.0000861			
Total	11	0.0142	0.00129			

Table B.11b:- Two way-ANOVA showing significance variation between seasons and stations for trace – metals in surface sediments.

Source of Variation	DF	SS	MS	F	P	F crit
Na						
Station	2	50.309	25.154	81.630	<0.001	3.635
Season	2	62.553	31.277	101.5	<0.001	3.635
Depth	4	0.647	0.162	0.525	0.719	3.01
Residual	16	4.930	0.308			
Total	44	139.3	3.166			
K						
Station	2	25.787	12.894	58.017	<0.001	3.635
Season	2	39.239	19.619	88.282	<0.001	3.635
Depth	4	0.553	0.138	0.622	0.653	3.01
Residual	16	3.556	0.222			
Total	44	94.087	2.138			
Mg						
Station	2	122.4	61.199	20.007	<0.001	3.635
Season	2	349.82	174.910	57.180	<0.001	3.635
Depth	5	3.495	0.699	0.229	0.946	3.01
Residual	20	61.18	3.059			
Total	53	713.68	13.466			

Table B.12a:- Three way-ANOVA showing significance variation between seasons stations and depth for major elements in core sediments.

Source of Variation	DF	SS	MS	F	P	F crit
Fe						
Station	2	0.0035	0.00173	25.567	<0.001	3.49
Season	2	0.0032	0.00158	23.253	<0.001	3.49
Depth	5	0.0007	0.000131	1.926	0.135	2.71
Residual	20	0.0014	0.0000678			
Total	53	0.0110	0.000208			
Mn						
Station	2	0.0827	0.0413	111.15	<0.001	3.49
Season	2	0.0170	0.00851	22.892	<0.001	3.49
Depth	5	0.0015	0.000292	0.785	0.573	2.71
Residual	20	0.0074	0.000372			
Total	53	0.130	0.00245			
Ni						
Station	2	0.0994	0.0497	89.378	<0.001	3.49
Season	2	0.148	0.0740	133.163	<0.001	3.49
Depth	5	0.0153	0.00307	5.521	0.002	2.71
Residual	20	0.0111	0.000556			
Total	53	0.312	0.00588			
Cu						
Station	2	0.006	0.00298	51.412	<0.001	3.49
Season	2	0.0023	0.00114	19.696	<0.001	3.49
Depth	5	0.00286	0.000572	9.860	<0.001	2.71
Residual	20	0.0012	0.0000580			
Total	53	0.0155	0.000292			

Zn						
Station	2	0.263	0.132	3.231	0.061	3.49
Season	2	0.532	0.266	6.536	0.007	3.49
Depth	5	0.252	0.0503	1.235	0.330	2.71
Residual	20	0.815	0.0407			
Total	53	3.380	0.0638			
Co						
Station	2	0.0018	0.000917	35.964	<0.001	3.49
Season	2	0.0003	0.000146	5.730	0.011	3.49
Depth	5	0.0002	0.0000296	1.160	0.363	2.71
Residual	20	0.0005	0.0000255			
Total	53	0.0035	0.0000653			
Pb						
Station	2	0.0042	0.00208	9.690	0.001	3.49
Season	2	0.0032	0.00159	7.413	0.004	3.49
Depth	5	0.0017	0.000342	1.596	0.207	2.71
Residual	20	0.0043	0.000214			
Total	53	0.0166	0.000312			
Cr						
Station	2	0.0858	0.0429	165.99	<0.001	3.49
Season	2	0.0839	0.0420	162.3	<0.001	3.49
Depth	5	0.0116	0.00233	8.994	<0.001	2.71
Residual	20	0.0052	0.000259			
Total	53	0.213	0.00402			

Table B.12b:- Three way-ANOVA showing significance variation between stations, seasons and depth for trace metals in core sediments.

Appendix C

CORRELATION COEFFICIENTS

	Temp.	pH	TSS	DH	S(‰)	DO	Alk
Temp.	1.000	.082	.302	.633(*)	.457	.185	-.024
pH	.082	1.000	.352	-.159	-.322	.737(**)	.630(*)
TSS	.302	.352	1.000	.133	-.111	.214	.296
DH	.633(*)	-.159	.133	1.000	.747(**)	-.100	-.011
S(‰)	.457	-.322	-.111	.747(**)	1.000	-.353	-.185
DO	.185	.737(**)	.214	-.100	-.353	1.000	.671(**)
Alk	-.024	.630(*)	.296	-.011	-.185	.671(**)	1.000

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.1a:- Correlation coefficients of various hydrographical parameters at Station 1

	Temp.	pH	TSS	DH	S(‰)	DO	Alk
Temp.	1.000	.560(*)	-.417	.381	.375	.591(*)	.192
pH	.560(*)	1.000	.164	.070	.285	.841(**)	.003
TSS	-.417	.164	1.000	-.330	-.215	.023	-.386
DH	.381	.070	-.330	1.000	.847(**)	.113	.019
S(‰)	.375	.285	-.215	.847(**)	1.000	.430	-.356
DO	.591(*)	.841(**)	.023	.113	.430	1.000	-.348
Alk	.192	.003	-.386	.019	-.356	-.348	1.000

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.1b:- Correlation coefficients of various hydrographical parameters at Station 2

	Temp.	pH	TSS	DH	S(‰)	DO	Alk
Temp.	1.000	.249	-.005	.400	.406	.362	-.042
pH	.249	1.000	.132	.415	.417	.266	.253
TSS	-.005	.132	1.000	-.271	-.285	.378	-.022
DH	.400	.415	-.271	1.000	.763(**)	-.217	-.261
S(‰)	.406	.417	-.285	.763(**)	1.000	-.265	-.233
DO	.362	.266	.378	-.217	-.265	1.000	.324
Alk	-.042	.253	-.022	-.261	-.233	.324	1.000

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.1c:- Correlation coefficients of various hydrographical parameters at Station 3

	Temp.	pH	TSS	DH	S(‰)	DO	Alk
Temp.	1.000	.607	.138	.471	.786(*)	-.280	-.355
pH	.607	1.000	.432	.915(**)	.498	-.473	-.028
TSS	.138	.432	1.000	.457	.029	.129	-.821(*)
DH	.471	.915(**)	.457	1.000	.600	-.500	-.072
S(‰)	.786(*)	.498	.029	.600	1.000	-.326	-.365
DO	-.280	-.473	.129	-.500	-.326	1.000	-.194
Alk	-.355	-.028	-.821(*)	-.072	-.365	-.194	1.000
*Correlation is significant at the 0.05 level.							
** Correlation is significant at the 0.01 level.							

Table C.1d:- Correlation coefficients of various hydrographical parameters at Station R -

	Temp.	pH	TSS	DH	S(‰)	DO	Alkalinity
Temp	1	-0.044	-0.529	-0.721	-0.679	0.067	-0.812
pH	-0.044	1	0.511	0.057	0.458	0.773	0.228
TSS	-0.529	0.511	1	0.874	.982(*)	0.778	0.906
DH	-0.721	0.057	0.874	1	0.913	0.405	.972(*)
S(‰)	-0.679	0.458	.982(*)	0.913	1	0.661	.962(*)
DO	0.067	0.773	0.778	0.405	0.661	1	0.44
Alkalinity	-0.812	0.228	0.906	.972(*)	.962(*)	0.44	1
* Correlation is significant at the 0.05 level (2-tailed).							
** Correlation is significant at the 0.01 level (2-tailed).							

Table C.2a:- Correlation coefficients of various hydrographical parameters during Premonsoon

	Temp.	pH	TSS	DH	S(‰)	DO	Alkalinity
Temp	1	-0.592	-0.067	-0.544	-0.764	0.859	-0.334
pH	-0.592	1	0.816	.996(**)	0.936	-0.808	0.924
TSS	-0.067	0.816	1	0.824	0.568	-0.324	0.819
DH	-0.544	.996(**)	0.824	1	0.934	-0.803	.955(*)
S(‰)	-0.764	0.936	0.568	0.934	1	-.963(*)	0.861
DO	0.859	-0.808	-0.324	-0.803	-.963(*)	1	-0.719
Alkalinity	-0.334	0.924	0.819	.955(*)	0.861	-0.719	1
* Correlation is significant at the 0.05 level (2-tailed).							
** Correlation is significant at the 0.01 level (2-tailed).							

Table C.2b:- Correlation coefficients of various hydrographical parameters during Monsoon

	Temp.	PH	TSS	DH	S(‰)	DO	Alkalinity
Temp	1	0.691	0.163	-0.499	-0.865	0.814	-0.006
pH	0.691	1	-0.575	0.268	-0.256	0.326	0.601
TSS	0.163	-0.575	1	-0.842	-0.547	0.319	-0.653
DH	-0.499	0.268	-0.842	1	0.863	-0.769	0.809
S(‰)	-0.865	-0.256	-0.547	0.863	1	-0.94	0.493
DO	0.814	0.326	0.319	-0.769	-0.94	1	-0.541
Alkalinity	-0.006	0.601	-0.653	0.809	0.493	-0.541	1
* Correlation is significant at the 0.05 level (2-tailed).							
** Correlation is significant at the 0.01 level (2-tailed).							

Table C.2c:- Correlation coefficients of various hydrographical parameters during Postmonsoon

	Temp.	pH	S(‰)	DO	Alk	Chl.	TSS	DH
Temp.	1.000	-.420	-.450	.801(**)	.438	.497	.350	-.865(*)
pH	-.420	1.000	.629	-.186	-.582	-.283	.346	.131
S(‰)	-.450	.629	1.000	-.555	-.422	-.302	-.208	.470
DO	.801(**)	-.186	-.555	1.000	.115	.111	.407	-.702
Alk	.438	-.582	-.422	.115	1.000	.620	-.145	-.195
Chl.	.497	-.283	-.302	.111	.620	1.000	.472	-.776
TSS	.350	.346	-.208	.407	-.145	.472	1.000	-.747
*Correlation is significant at the 0.05 level. ** Correlation is significant at the 0.01 level.								

Table C.3a:- Diurnal correlation coefficients of various hydrographical parameters at Station 1

	Temp.	pH	S(‰)	DO	Alk	Chl.	TSS	DH
Temp.	1.000	.843(**)	-.126	.926(**)	.593	.787(*)	.553	.267
pH	.843(**)	1.000	.000	.925(**)	.680(*)	.476	.476	.336
S(‰)	-.126	.000	1.000	.161	-.311	-.291	.014	-.650
DO	.926(**)	.925(**)	.161	1.000	.556	.659	.527	.149
Alk	.593	.680(*)	-.311	.556	1.000	.527	.037	.922(**)
Chl.	.787(*)	.476	-.291	.659	.527	1.000	.254	.652
TSS	.553	.476	.014	.527	.037	.254	1.000	-.419
DH	.267	.336	-.650	.149	.922(**)	.652	-.419	1.000
*Correlation is significant at the 0.05 level. ** Correlation is significant at the 0.01 level.								

Table C.3b:- Diurnal correlation coefficients of various hydrographical parameters at Station 2

	Temp.	pH	S(‰)	DO	Alk	Chl.	TSS	DH
Temp.	1.000	-.069	-.644	.161	-.168	.693(*)	-.145	-.840(*)
pH	-.069	1.000	-.041	-.290	.272	.045	.396	-.255
S(‰)	-.644	-.041	1.000	-.086	.114	-.567	.606	.825(*)
DO	.161	-.290	-.086	1.000	-.960(**)	.282	-.059	-.507
Alk	-.168	.272	.114	-.960(**)	1.000	-.154	-.026	.592
Chl.	.693(*)	.045	-.567	.282	-.154	1.000	-.368	-.545
TSS	-.145	.396	.606	-.059	-.026	-.368	1.000	.130
DH	-.840(*)	-.255	.825(*)	-.507	.592	-.545	.130	1.000

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.3c:- Diurnal correlation coefficients of various hydrographical parameters at Station R

	DHS	DP	MCHO	PCHO	DT&L	DTL	DTAA	DFAA	DCAA
Temp.	-.015	.459	-.563(*)	.029	-.410	-.170	.260	-.161	.273
PH	.070	-.168	-.373	.460	-.377	.448	-.468	-.122	-.454
TSS	.188	.551(*)	-.229	-.101	-.017	.223	.378	.023	.374
DH	-.062	.691(**)	-.470	-.034	-.313	-.341	.267	-.257	.288
S(‰)	.112	.497	-.051	-.300	-.116	-.449	.240	-.137	.251
DO	.252	-.211	-.538(*)	.515(*)	-.347	.650(**)	-.606(*)	-.178	-.585(*)
Alk	.157	-.135	-.529(*)	.382	-.326	.110	-.628(*)	.109	-.633(*)
POC	.017	.627(**)	-.185	-.209	.032	.046	.477	.029	.471
DHS	1.000	.031	.204	-.320	.092	.223	-.105	-.080	-.096
DP	.031	1.000	-.300	-.202	-.061	-.241	.769(**)	-.057	.768(**)
MCHO	.204	-.300	1.000	-.597(*)	.729(**)	-.223	.221	.231	.198
PCHO	-.320	-.202	-.597(*)	1.000	-.360	.376	-.532(*)	.045	-.532(*)
T&L	.092	-.061	.729(**)	-.360	1.000	-.083	.258	.466	.213
DTL	.223	-.241	-.223	.376	-.083	1.000	-.387	-.177	-.368
DTAA	-.105	.769(**)	.221	-.532(*)	.258	-.387	1.000	-.034	.996(**)
DFAA	-.080	-.057	.231	.045	.466	-.177	-.034	1.000	-.126
DCAA	-.096	.768(**)	.198	-.532(*)	.213	-.368	.996(**)	-.126	1.000

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table 3. 2.11a:- Correlation coefficients of dissolved organic constituents at Station 1

	DHS	DP	MCHO	PCHO	DT&L	DTL	DTAA	DFAA	DCAA
Temp.	.082	.403	-.178	.340	-.458	-.017	.221	-.219	.236
pH	.083	.256	.479	.020	.137	.061	.381	.556(*)	.368
TSS	.059	-.317	.573(*)	-.260	.576(*)	.021	.232	.441	.219
DH	.334	.552(*)	-.132	-.162	-.333	-.255	-.284	-.100	-.288
S(‰)	.327	.412	.212	-.092	-.082	-.276	.011	.237	.001
DO	-.041	.256	.476	-.049	-.097	-.278	.439	.442	.432
Alk	.251	.213	-.281	.213	-.109	.632(*)	-.185	-.330	-.176
POC	.144	.027	.278	-.274	.434	.370	-.012	.306	-.026
DHS	1.000	-.148	.236	-.190	.340	.174	-.048	.044	-.051
DP	-.148	1.000	-.269	.094	-.333	.046	.215	.253	.211
MCHO	.236	-.269	1.000	-.140	.561(*)	.190	.505	.594(*)	.494
PCHO	-.190	.094	-.140	1.000	-.218	.266	.370	.063	.378
T&L	.340	-.333	.561(*)	-.218	1.000	.144	.254	.537(*)	.238
DTL	.174	.046	.190	.266	.144	1.000	.205	.161	.204
DTAA	-.048	.215	.505	.370	.254	.205	1.000	.714(**)	.999(**)
DFAA	.044	.253	.594(*)	.063	.537(*)	.161	.714(**)	1.000	.691(**)
DCAA	-.051	.211	.494	.378	.238	.204	.999(**)	.691(**)	1.000

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.4b:- Correlation coefficients of dissolved organic constituents at Station 2

	DHS	DP	MCHO	PCHO	DT&L	DTL	DTAA	DFAA	DCAA
Temp.	-.294	.317	.047	-.057	-.326	-.237	-.015	.261	-.036
pH	-.122	.621(*)	-.141	.598(*)	-.176	.130	.331	-.128	.340
TSS	-.211	-.220	.013	.277	-.287	-.248	.871(**)	.049	.873(**)
DH	.125	.636(**)	-.402	.106	-.268	-.321	.062	.132	.055
S(‰)	.132	.813(**)	-.317	.031	.235	-.033	-.020	.309	-.039
DO	-.393	-.162	.109	.534(*)	-.330	.135	.238	.351	.218
Alk	-.062	.015	.139	.293	-.134	.623(*)	-.064	-.388	-.048
POC	-.225	.372	-.231	-.092	.168	.070	.315	.581(*)	.282
DHS	1.000	-.168	-.109	-.487	.045	-.029	-.393	-.443	-.369
DP	-.168	1.000	-.336	.252	.263	.151	.151	.198	.140
MCHO	-.109	-.336	1.000	-.285	.272	.179	-.011	-.274	.006
PCHO	-.487	.252	-.285	1.000	-.339	.146	.553	.262	.540
T&L	.045	.263	.272	-.339	1.000	.445	-.321	.187	-.334
DTL	-.029	.151	.179	.146	.445	1.000	-.362	.073	-.369
DTAA	-.393	.151	-.011	.553	-.321	-.362	1.000	.123	.998(**)
DFAA	-.443	.198	-.274	.262	.187	.073	.123	1.000	.064
DCAA	-.369	.140	.006	.540	-.334	-.369	.998(**)	.064	1.000

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.4c:- Correlation coefficients of dissolved organic constituents at Station 3

	DHS	DP	MCHO	PCHO	DT&L	DTL	DTAA	DFAA	DCAA
Temp.	-.540	.791(*)	-.257	-.677	-.457	.107	.529	-.139	.530
pH	-.296	.632	.220	-.400	.047	.232	.499	.346	.484
TSS	.109	-.168	.643	-.255	.575	.183	-.318	.519	-.333
DH	.077	.511	.460	-.165	.263	.136	.272	.434	.255
S(‰)	-.024	.698(*)	.026	-.504	-.209	-.188	.291	-.133	.293
DO	-.108	-.551	-.164	-.237	-.082	-.054	-.653	.276	-.658
Alk	.039	.055	-.265	.659	-.320	.409	.240	.416	.230
POC	.004	.505	.611	-.261	.409	.517	.307	.446	.290
DHS	1.000	-.479	.654	.606	.585	-.299	-.659	.135	-.659
DP	-.479	1.000	-.138	-.584	-.298	.287	.868(**)	-.041	.864(**)
DMCHO	.654	-.138	1.000	.209	.913(**)	.217	-.309	.630	-.327
DPCHO	.606	-.584	.209	1.000	.267	.208	-.597	.188	-.608
DT&L	.585	-.298	.913(**)	.267	1.000	.212	-.322	.518	-.337
DTL	-.299	.287	.217	.208	.212	1.000	.319	.674	.295
DTAA	-.659	.868(**)	-.309	-.597	-.322	.319	1.000	-.189	.999(**)
DFAA	.135	-.041	.630	.188	.518	.674	-.189	1.000	-.220
DCAA	-.659	.864(**)	-.327	-.608	-.337	.295	.999(**)	-.220	1.000

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.4d:- Correlation coefficients of dissolved organic constituents at Station R

	DHS	DP	DMCHO	DPCHO	DT&L	DL	DTAA	DCAA	DFAA
temp	-0.551	-.954(*)	-0.177	0.759	-0.945	-0.938	-.988(*)	-.991(**)	0.395
pH	0.173	-0.133	0.573	0.383	0.173	0.361	0.184	0.159	0.863
TSS	0.934	0.589	-0.189	0.149	0.772	0.558	0.555	0.539	0.4
DH	.970(*)	0.852	-0.416	-0.191	0.892	0.59	0.679	0.676	-0.084
S(‰)	0.927	0.718	-0.118	-0.038	0.876	0.692	0.699	0.686	0.263
DO	0.593	-0.047	-0.077	0.688	0.226	0.1	0.01	-0.015	0.873
Alk.	0.929	0.875	-0.192	-0.26	.957(*)	0.748	0.8	0.794	-0.009
POC	0.205	0.746	0.559	-0.82	0.764	.954(*)	0.941	0.943	-0.325
DHS	1	0.7	-0.48	0.055	0.785	0.453	0.521	0.514	0.125
DP	0.7	1	-0.127	-0.675	.951(*)	0.805	0.905	0.911	-0.468
DMCHO	-0.48	-0.127	1	-0.301	0.002	0.456	0.298	0.289	0.221
DPCHO	0.055	-0.675	-0.301	1	-0.513	-0.646	-0.718	-0.735	0.797
DT&L	0.785	.951(*)	0.002	-0.513	1	0.888	0.937	0.934	-0.18
DL	0.453	0.805	0.456	-0.646	0.888	1	.979(*)	.975(*)	-0.124
DTAA	0.521	0.905	0.298	-0.718	0.937	.979(*)	1	1.000(**)	-0.28
DCAA	0.514	0.911	0.289	-0.735	0.934	.975(*)	1.000(**)	1	-0.306
DFAA	0.125	-0.468	0.221	0.797	-0.18	-0.124	-0.28	-0.306	1

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.5a:- Correlation coefficients of dissolved organic constituents during premonsoon

	DHS	DP	DMCHO	DPCHO	DT&L	DL	DTAA	DCAA	DFAA
temp	-0.815	0.001	-0.468	-0.721	-0.495	-0.51	0.188	0.216	-0.752
pH	0.931	0.782	0.874	0.891	.993(**)	.994(**)	0.655	0.63	0.847
TSS	0.633	0.875	0.87	0.703	0.869	0.847	.967(*)	.960(*)	0.42
DH	0.898	0.828	0.839	0.846	.996(**)	.999(**)	0.675	0.65	0.857
S(‰)	0.919	0.638	0.688	0.806	0.901	0.918	0.369	0.337	.976(*)
DO	-0.85	-0.443	-0.507	-0.698	-0.751	-0.777	-0.106	-0.072	-.983(*)
Alk.	0.729	0.941	0.69	0.653	.951(*)	.960(*)	0.727	0.704	0.82
POC	0.703	0.831	0.921	0.777	0.888	0.865	0.936	0.927	0.449
DHS	1	0.502	0.871	.970(*)	0.886	0.884	0.416	0.39	0.821
DP	0.502	1	0.604	0.467	0.845	0.847	0.867	0.852	0.586
DMCHO	0.871	0.604	1	0.95	0.871	0.846	0.734	0.721	0.513
DPCHO	.970(*)	0.467	0.95	1	0.854	0.84	0.506	0.486	0.664
DT&L	0.886	0.845	0.871	0.854	1	.999(**)	0.732	0.708	0.809
DL	0.884	0.847	0.846	0.84	.999(**)	1	0.707	0.682	0.837
DTAA	0.416	0.867	0.734	0.506	0.732	0.707	1	.999(**)	0.228
DCAA	0.39	0.852	0.721	0.486	0.708	0.682	.999(**)	1	0.194
DFAA	0.821	0.586	0.513	0.664	0.809	0.837	0.228	0.194	1

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.5b:- Correlation coefficients of dissolved organic constituents during monsoon

	DHS	DP	DMCHO	DPCHO	DT&L	DL	DTAA	DCAA	DFAA
temp	-0.914	0.705	-0.597	0.854	-.972(*)	-0.639	0.73	0.731	-0.693
pH	-0.514	.987(*)	-.975(*)	0.895	-0.713	-0.494	.996(**)	.996(**)	-0.948
TSS	-0.207	-0.502	0.592	-0.342	-0.044	-0.236	-0.545	-0.544	0.423
DH	0.66	0.262	-0.397	-0.122	0.477	0.122	0.199	0.201	-0.261
S(‰)	0.93	-0.257	0.115	-0.591	0.852	0.389	-0.322	-0.321	0.239
DO	-.976(*)	0.274	-0.138	0.704	-0.882	-0.13	0.406	0.403	-0.202
Alk.	0.345	0.66	-0.754	0.18	0.082	-0.477	0.525	0.53	-0.711
POC	0.452	-.981(*)	.966(*)	-0.778	0.672	0.761	-0.918	-0.921	.998(**)
DHS	1	-0.475	0.347	-0.825	.964(*)	0.289	-0.583	-0.581	0.412
DP	-0.475	1	-.990(*)	0.846	-0.69	-0.62	.974(*)	.976(*)	-.987(*)
DMCHO	0.347	-.990(*)	1	-0.778	0.581	0.587	-.951(*)	-.953(*)	.980(*)
DPCHO	-0.825	0.846	-0.778	1	-0.924	-0.342	0.932	0.93	-0.77
DT&L	.964(*)	-0.69	0.581	-0.924	1	0.451	-0.765	-0.764	0.64
DL	0.289	-0.62	0.587	-0.342	0.451	1	-0.462	-0.468	0.73
DTAA	-0.583	.974(*)	-.951(*)	0.932	-0.765	-0.462	1	1.000(**)	-0.925
DCAA	-0.581	.976(*)	-.953(*)	0.93	-0.764	-0.468	1.000(**)	1	-0.928
DFAA	0.412	-.987(*)	.980(*)	-0.77	0.64	0.73	-0.925	-0.928	1

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.5c:- Correlation coefficients of dissolved organic constituents in during postmonsoon

	DP	DMCHO	DPCHO	T&L	DTL	DHS
Temp.	-.637	-.125	.033	-.622	.081	-.596
PH	.263	-.057	-.234	.710(*)	.473	.175
S(‰)	.241	-.328	.095	.437	.711(*)	.358
DO	-.504	-.140	-.055	-.395	-.086	-.531
Alk	-.417	.036	.319	-.567	-.264	.030
Chl.	-.695(*)	-.080	-.163	-.622	.107	-.683
TSS	-.294	-.174	-.733(*)	-.003	.309	-.735
DH	.702	.266	.673	.392	-.310	.845(*)
POC	-.464	.162	-.639	-.399	.487	-.560
DP	1.000	.402	-.132	.847(**)	-.155	.710
DMCHO	.402	1.000	.294	.318	-.677(*)	.618
DPCHO	-.132	.294	1.000	-.245	-.385	.785
DT&L	.847(**)	.318	-.245	1.000	.119	.509
DTL	-.155	-.677(*)	-.385	.119	1.000	-.381
DHS	.710	.618	.785	.509	-.381	1.000

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.-

Table C.6a:- Diurnal correlation coefficients of dissolved organic constituents at Station 1

	DP	DMCHO	DPCHO	T&L	DTL	DHS
Temp.	-.472	.349	.212	-.556	-.411	-.050
PH	-.622	.319	.195	-.672(*)	-.637	.047
S(‰)	.221	.378	.611	.278	.061	-.688
DO	-.421	.469	.300	-.483	-.505	-.164
Alk	-.550	.348	.065	-.770(*)	-.878(**)	.771
Chl.	-.042	.449	-.044	-.222	-.345	.380
TSS	-.466	-.379	-.122	-.140	-.005	-.608
DH	-.359	.209	-.201	-.637	-.848(*)	.934(**)
POC	-.241	-.178	.050	.208	.195	-.180
DP	1.000	.354	-.272	.892(**)	.587	-.116
DMCHO	.354	1.000	.369	-.012	-.260	.175
DPCHO	-.272	.369	1.000	-.386	-.208	-.348
DT&L	.892(**)	-.012	-.386	1.000	.724(*)	-.427
DTL	.587	-.260	-.208	.724(*)	1.000	-.616
DHS	-.116	.175	-.348	-.427	-.616	1.000

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.6b:- Diurnal correlation coefficients of dissolved organic constituents at Station 2

	DP	DMCHO	DPCHO	T&L	DTL	DHS
Temp.	-.674(*)	.336	.304	-.117	-.101	.395
pH	-.073	.003	-.203	.281	.274	.412
S(‰)	.545	-.287	-.103	-.417	.067	-.452
DO	-.468	.345	.136	.399	-.699(*)	.092
Alk	.508	-.315	.014	-.457	.795(*)	-.096
Chl.	-.416	.757(*)	.731(*)	.124	-.148	.776
TSS	-.175	-.103	-.455	-.334	-.202	-.068
DH	.968(**)	-.124	.011	-.036	.057	-.129
POC	.089	.115	-.014	-.625	-.141	.530
DP	1.000	-.288	.232	-.129	.523	-.320
DMCHO	-.288	1.000	.580	.199	-.559	.933(**)
DPCHO	.232	.580	1.000	.030	.047	.663
DT&L	-.129	.199	.030	1.000	-.352	.283
DTL	.523	-.559	.047	-.352	1.000	-.747
DHS	-.320	.933(**)	.663	.283	-.747	1.000

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.6c:- Diurnal correlation coefficients of dissolved organic constituents at Station R

	PP	PT&L	PTCHO	PMCHO	PPCHO	POC	PTL	PHA	PTAA	PFAA	PCAA
PP	1.000	.755(**)	.742(**)	.407	.792(**)	.403	.598(*)	.705(*)	.477	.200	.615(*)
PT&L	.755(**)	1.000	.862(**)	.781(**)	.602(*)	.453	.533	.869(**)	.673(*)	.500	.682(*)
PTCHO	.742(**)	.862(**)	1.000	.811(**)	.796(**)	.685(*)	.790(**)	.816(**)	.639(*)	.571	.593
PMCHO	.407	.781(**)	.811(**)	1.000	.291	.643(*)	.613(*)	.767(**)	.569	.857(**)	.213
PPCHO	.792(**)	.602(*)	.796(**)	.291	1.000	.455	.658(*)	.540	.516	.047	.619(*)
POC	.403	.453	.685(*)	.643(*)	.455	1.000	.912(**)	.322	.305	.660(*)	-.089
PTL	.598(*)	.533	.790(**)	.613(*)	.658(*)	.912(**)	1.000	.484	.393	.540	.218
PHA	.705(*)	.869(**)	.816(**)	.767(**)	.540	.322	.484	1.000	.660(*)	.488	.911(**)
PTAA	.477	.673(*)	.639(*)	.569	.516	.305	.393	.660(*)	1.000	.246	.704(*)
PFAA	.200	.500	.571	.857(**)	.047	.660(*)	.540	.488	.246	1.000	-.515
PCAA	.615(*)	.682(*)	.593	.213	.619(*)	-.089	.218	.911(**)	.704(*)	-.515	1.000
Temp	-.611(*)	-.256	-.314	.084	-.601(*)	-.110	-.175	-.216	-.481	.053	-.307
pH	.487	.305	.261	-.061	.489	-.289	.034	.432	.229	-.395	.795(**)
TSS	.371	.728(**)	.690(*)	.823(**)	.277	.340	.493	.808(**)	.333	.561	.640(*)
DH	-.360	-.077	-.092	.241	-.400	.203	-.011	-.313	-.360	.211	-.517
S(‰)	-.530	-.258	-.325	.021	-.553	.059	-.221	-.483	-.060	.122	-.494
DO	.136	.116	.025	-.221	.270	-.432	-.207	.242	.194	-.456	.682(*)
Alk	.629(*)	.518	.134	-.213	.257	-.297	-.019	.603(*)	.333	-.465	.635(*)

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.7a:- Correlation coefficients of various constituents in particulate matter at Station 1

	PP	PT&L	PTCHO	PMCHO	PPCHO	POC	PTL	PHA	PTAA	PFAA	PCAA
PP	1.000	.823(**)	.963(**)	.767(**)	.918(**)	.730(**)	.715(**)	.954(**)	.749(**)	.474	.689(*)
PT&L	.823(**)	1.000	.847(**)	.391	.943(**)	.814(**)	.974(**)	.936(**)	.645(*)	.656(*)	.489
PTCHO	.963(**)	.847(**)	1.000	.791(**)	.957(**)	.779(**)	.751(**)	.944(**)	.811(**)	.567	.724(**)
PMCHO	.767(**)	.391	.791(**)	1.000	.580(*)	.510	.232	.594(*)	.752(**)	.354	.743(**)
PPCHO	.918(**)	.943(**)	.957(**)	.580(*)	1.000	.796(**)	.891(**)	.976(**)	.724(**)	.588(*)	.612(*)
POC	.730(**)	.814(**)	.779(**)	.510	.796(**)	1.000	.787(**)	.758(**)	.732(**)	.876(**)	.500
PTL	.715(**)	.974(**)	.751(**)	.232	.891(**)	.787(**)	1.000	.872(**)	.583(*)	.650(*)	.418
PHA	.954(**)	.936(**)	.944(**)	.594(*)	.976(**)	.758(**)	.872(**)	1.000	.695(*)	.540	.597(*)
PTAA	.749(**)	.645(*)	.811(**)	.752(**)	.724(**)	.732(**)	.583(*)	.695(*)	1.000	.587(*)	.940(**)
PFAA	.474	.656(*)	.567	.354	.588(*)	.876(**)	.650(*)	.540	.587(*)	1.000	.275
PCAA	.689(*)	.489	.724(**)	.743(**)	.612(*)	.500	.418	.597(*)	.940(**)	.275	1.000
Temp	.079	-.048	.088	.163	.040	-.233	-.020	.076	.032	-.227	.134
pH	.327	.232	.222	.126	.236	.076	.283	.357	.371	-.037	.456
TSS	.783(**)	.325	.741(**)	.879(**)	.570	.313	.160	.601(*)	.593(*)	.042	.686(*)
DH	.104	-.167	.151	.393	.014	.054	-.219	-.037	.295	.152	.286
S(‰)	.189	-.096	.246	.563	.061	.221	-.139	.027	.507	.330	.463
DO	.404	-.080	.293	.228	.248	-.023	.677(*)	.641(*)	.195	.050	.189
Alk	.754(**)	.688(*)	.634(*)	.179	.693(*)	.398	.663(*)	.756(**)	.333	.133	.344

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level..

Table C.7b:- Correlation coefficients of various constituents in particulate organic matter at Station 2

	PP	PT&L	PTCHO	PMCHO	PPCHO	POC	PTL	PHA	PTAA	PFAA	PCAA
PP	1.000	-.122	-.317	-.367	-.271	.360	-.576(*)	.166	.435	-.525	.724(*)
PT&L	-.122	1.000	.641(*)	.431	.684(*)	.799(**)	.523	698(*)	.242	.424	.028
PTCHO	-.317	.641(*)	1.000	.876(**)	.978(**)	.535	.729(**)	.108	.233	740(**)	.215
PMCHO	-.367	.431	.876(**)	1.000	.755(**)	.419	.626(*)	-.122	.449	713(**)	.138
PPCHO	-.271	.684(*)	.978(**)	.755(**)	1.000	.545	.718(**)	.200	.027	.695(*)	.203
POC	.360	.799(**)	.535	.419	.545	1.000	.140	622(*)	.485	.183	.355
PTL	-.576(*)	.523	.729(**)	.626(*)	.718(**)	.140	1.000	-.094	.330	894(**)	-.450
PHA	.166	.698(*)	.108	-.122	.200	.622(*)	-.094	1.000	-.125	-.100	-.070
PTAA	.435	.242	.233	.449	.027	.485	.330	-.125	1.000	.376	.422
PFAA	-.525	.424	.740(**)	.713(**)	.695(*)	.183	.894(**)	-.100	.376	1.000	-.681(*)
PCAA	724(*)	.028	.215	.138	.203	.355	-.450	-.070	.422	-.681(*)	1.000
Temp	-.326	.293	.736(**)	.768(**)	.665(*)	.238	.547	-.008	-.064	703(*)	-.315
pH	-.326	-.222	.190	.213	.165	-.298	.171	-.327	-.201	.154	.074
TSS	-.003	-.244	.159	.351	.064	-.108	.047	-.310	.350	.181	.477
DH	-.285	.375	.435	.388	.422	.292	.168	.115	-.008	.019	.138
S(‰)	-.511	.535	.552	.532	.519	.390	.374	.376	-.004	.441	-.412
DO	-.272	-.065	.491	.441	.475	-.243	.674(*)	-.534	-.032	624(*)	.035
Alk	.415	-.662(*)	-.399	-.099	-.475	-.382	-.482	-.474	-.065	-.147	.213

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.7c:- Correlation coefficients of various constituents in particulate matter at Station 3

	PP	PT&L	PTCHO	PMCHO	PPCHO	POC	PTL	PHA	PTAA	PFAA	PCAA
PP	1.000	.285	.137	-.106	.296	-.189	.501	.375	.064	.405	-.060
PT&L	.285	1.000	.868(**)	.473	.968(**)	.739(*)	.941(**)	.982(**)	.661(*)	.941(**)	-.044
PTCHO	.137	.868(**)	1.000	.825(**)	.894(**)	.646(*)	.812(**)	.882(**)	.539	.739(*)	.040
PMCHO	-.106	.473	.825(**)	1.000	.485	.464	.367	.509	.254	.280	.093
PPCHO	.296	.968(**)	.894(**)	.485	1.000	.632	.966(**)	.963(**)	.632(*)	.923(**)	-.154
POC	-.189	.739(*)	.646(*)	.464	.632	1.000	.490	.660(*)	.422	.576	-.064
PTL	.501	.941(**)	.812(**)	.367	.966(**)	.490	1.000	.961(**)	.641(*)	.959(**)	-.179
PHA	.375	.982(**)	.882(**)	.509	.963(**)	.660(*)	.961(**)	1.000	.649(*)	.951(**)	-.311
PTAA	.064	.661(*)	.539	.254	.632(*)	.422	.641(*)	.649(*)	1.000	.724(*)	.842(**)
PFAA	.405	.941(**)	.739(*)	.280	.923(**)	.576	.959(**)	.951(**)	.724(*)	1.000	-.414
PCAA	-.060	-.044	.040	.093	-.154	-.064	-.179	-.311	.842(**)	-.414	1.000
Temp	-.605	-.100	.078	.306	-.122	.487	-.329	-.165	-.067	-.304	.229
pH	-.136	.390	.610	.669(*)	.414	.509	.304	.439	.266	.295	.048
TSS	.010	.780(**)	.914(**)	.704(*)	.858(**)	.577	.730(*)	.747(*)	.410	.608	.074
DH	-.235	.408	.670(*)	.799(**)	.403	.430	.310	.471	.381	.328	.061
S(‰)	-.772(**)	-.124	.112	.472	-.200	.330	-.375	-.160	.063	-.310	.356
DO	.226	-.164	.109	.379	-.131	-.373	-.089	-.141	-.238	-.249	.120
Alk	.686(*)	-.328	-.532	-.410	-.599	-.217	.250	.411	.080	.509	-.027

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.7d:- Correlation coefficients of various constituents in particulate matter at Station R

	PP	PT&L	PTCHO	PMCHO	PPCHO	POC	PTL	PHS	PTAA	PFAA	PCAA
temp	-0.491	-0.441	-0.201	-0.824	0.583	-.997(**)	-0.232	-0.195	-0.58	-0.786	-0.479
pH	0.608	0.405	0.48	0.258	0.415	0.12	0.58	0.104	0.547	-0.372	0.653
TSS	.993(**)	.984(*)	0.932	0.906	0.38	0.577	0.948	0.827	.996(**)	0.541	.985(*)
DH	0.815	0.889	0.751	.960(*)	0.063	0.733	0.727	0.818	0.864	0.879	0.783
S(‰)	.969(*)	0.948	0.85	.965(*)	0.2	0.72	0.872	0.755	.990(**)	0.637	.959(*)
DO	0.826	0.778	0.891	0.444	0.809	0.003	0.921	0.673	0.759	-0.076	0.84
Alk.	0.866	0.879	0.727	.999(**)	-0.013	0.834	0.732	0.714	0.916	0.817	0.846
PP	1	.965(*)	0.928	0.87	0.412	0.545	.956(*)	0.78	.994(**)	0.447	.998(**)
PT&L	.965(*)	1	.966(*)	0.871	0.466	0.483	.961(*)	0.914	.964(*)	0.567	0.948
PTCHO	0.928	.966(*)	1	0.717	0.677	0.251	.992(**)	0.923	0.9	0.367	0.917
PMCHO	0.87	0.871	0.717	1	-0.028	0.848	0.728	0.69	0.92	0.8	0.853
PPCHO	0.412	0.466	0.677	-0.028	1	-0.536	0.654	0.595	0.319	-0.319	0.414
POC	0.545	0.483	0.251	0.848	-0.536	1	0.288	0.218	0.629	0.76	0.537
PTL	.956(*)	.961(*)	.992(**)	0.728	0.654	0.288	1	0.869	0.925	0.317	.951(*)
PHS	0.78	0.914	0.923	0.69	0.595	0.218	0.869	1	0.774	0.569	0.748
PTAA	.994(**)	.964(*)	0.9	0.92	0.319	0.629	0.925	0.774	1	0.535	.989(*)
PFAA	0.447	0.567	0.367	0.8	-0.319	0.76	0.317	0.569	0.535	1	0.403
PCAA	.998(**)	0.948	0.917	0.853	0.414	0.537	.951(*)	0.748	.989(*)	0.403	1

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.8a:- Correlation coefficients of various constituents in particulate matter during premonsoon

	PP	PT&L	PTCHO	PMCHO	PPCHO	POC	PTL	PHS	PTAA	PFAA	PCAA
Temp	-0.087	-0.115	-0.258	-0.308	-0.245	-0.217	-0.074	-0.398	-0.616	0.014	-0.805
pH	0.834	0.839	0.929	0.949	0.922	0.896	0.826	0.89	.982(*)	0.735	.952(*)
TSS	.999(**)	.999(**)	.966(*)	0.933	.973(*)	.988(*)	.999(**)	0.92	0.827	.988(*)	0.606
DH	0.844	0.842	0.939	.964(*)	0.931	0.898	0.836	0.865	.963(*)	0.736	0.936
S(‰)	0.597	0.598	0.755	0.81	0.74	0.686	0.585	0.691	0.888	0.451	.984(*)
DO	-0.358	-0.359	-0.55	-0.623	-0.53	-0.463	-0.344	-0.493	-0.75	-0.194	-0.933
Alk.	0.844	0.826	0.931	.964(*)	0.921	0.871	0.837	0.748	0.846	0.72	0.818
PP	1	.998(**)	.976(*)	0.947	.981(*)	.991(**)	1.000(**)	0.918	0.838	.980(*)	0.628
PT&L	.998(**)	1	.972(*)	0.941	.978(*)	.993(**)	.998(**)	0.937	0.852	.984(*)	0.639
PTCHO	.976(*)	.972(*)	1	.994(**)	1.000(**)	.990(**)	.973(*)	0.92	0.912	0.916	0.77
PMCHO	0.947	0.941	.994(**)	1	.990(**)	.969(*)	0.943	0.889	0.916	0.867	0.81
PPCHO	.981(*)	.978(*)	1.000(**)	.990(**)	1	.994(**)	.978(*)	0.926	0.909	0.926	0.758
POC	.991(**)	.993(**)	.990(**)	.969(*)	.994(**)	1	.990(*)	.952(*)	0.902	.958(*)	0.722
PTL	1.000(**)	.998(**)	.973(*)	0.943	.978(*)	.990(*)	1	0.915	0.831	.982(*)	0.617
PHS	0.918	0.937	0.92	0.889	0.926	.952(*)	0.915	1	0.945	0.908	0.772
PTAA	0.838	0.852	0.912	0.916	0.909	0.902	0.831	0.945	1	0.768	0.936
PFAA	.980(*)	.984(*)	0.916	0.867	0.926	.958(*)	.982(*)	0.908	0.768	1	0.507
PCAA	0.628	0.639	0.77	0.81	0.758	0.722	0.617	0.772	0.936	0.507	1

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table 4.22 b:- Correlation coefficients of various constituents in particulate matter during monsoon

	PP	PT&L	PTCHO	PMCHO	PPCHO	POC	PTL	PHS	PTAA	PFAA	PCAA
temp	-0.922	-0.664	-0.868	-0.226	-0.907	-0.751	-0.852	-0.454	-0.941	-.965(*)	-0.873
pH	-0.817	-.996(**)	-0.748	0.122	-0.873	-0.945	-0.682	-0.92	-0.7	-0.602	-0.852
TSS	0.008	0.62	-0.066	-0.638	0.111	0.359	-0.15	0.802	-0.002	-0.179	0.275
DH	0.197	-0.283	0.18	0.282	0.121	-0.177	0.227	-0.431	0.47	0.602	0.206
S(‰)	0.629	0.238	0.578	0.226	0.582	0.321	0.59	0.047	0.838	0.919	0.651
DO	-0.527	-0.339	-0.424	0.119	-0.509	-0.276	-0.408	-0.24	-0.903	-0.933	-0.765
Alk.	-0.366	-0.57	-0.413	-0.167	-0.415	-0.651	-0.381	-0.534	0.13	0.215	-0.092
PP	1	0.772	.986(*)	0.379	.994(**)	0.928	.968(*)	0.538	0.786	0.795	0.787
PT&L	0.772	1	0.69	-0.212	0.834	0.911	0.618	.950(*)	0.705	0.595	0.865
PTCHO	.986(*)	0.69	1	0.521	.969(*)	0.908	.995(**)	0.431	0.682	0.71	0.672
PMCHO	0.379	-0.212	0.521	1	0.295	0.209	0.597	-0.489	-0.11	0.034	-0.245
PPCHO	.994(**)	0.834	.969(*)	0.295	1	.956(*)	0.942	0.623	0.796	0.785	0.823
POC	0.928	0.911	0.908	0.209	.956(*)	1	0.867	0.746	0.649	0.6	0.755
PTL	.968(*)	0.618	.995(**)	0.597	0.942	0.867	1	0.343	0.643	0.687	0.612
PHS	0.538	.950(*)	0.431	-0.489	0.623	0.746	0.343	1	0.585	0.437	0.789
PTAA	0.786	0.705	0.682	-0.11	0.796	0.649	0.643	0.585	1	.983(*)	.960(*)
PFAA	0.795	0.595	0.71	0.034	0.785	0.6	0.687	0.437	.983(*)	1	0.897
PCAA	0.787	0.865	0.672	-0.245	0.823	0.755	0.612	0.789	.960(*)	0.897	1

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table 4.22 c:- Correlation coefficients of various constituents in particulate matter during postmonsoon

	PP	PT&L	PTCHO	PMCHO	POC	PTL	PHS	PFAA	DO	PPCHO
Temp.	-.438	-.285	.683	.178	.671	.304	-.165	.463	.764	.417
pH	.161	-.161	-.078	.254	-.627	.914	.845	.341	-.080	-.497
S(‰)	.108	.269	-.617	-.297	-.300	-.538	-.768	-.870	-.645	-.152
Alk.	-.616	-.457	.515	.183	.327	.537	-.322	.250	.710	.233
Chl.	.601	.671	.510	.318	.903(*)	-.483	-.033	.329	-.108	.006
TSS	.193	.135	.337	-.002	.511	-.040	.452	.503	.246	.352
DH	-.777	-.667	-.692	-.520	-.979(*)	.312	-.070	-.504	-.050	.120
PP	1.000	.946(*)	.094	.439	.346	-.793	.027	-.009	-.753	-.622
PT&L	.946(*)	1.000	.053	.313	.501	-.867	-.281	-.185	-.773	-.458
PTCHO	.094	.053	1.000	.813	.657	.376	.319	.869	.542	-.296
PMCHO	.439	.313	.813	1.000	.365	.337	.365	.702	.096	-.797
POC	.346	.501	.657	.365	1.000	-.425	-.257	.336	.122	.083
PTL	-.793	-.867	.376	.337	-.425	1.000	.832	.663	.922	-.187
PHS	.027	-.281	.319	.365	-.257	.832	1.000	.736	.334	-.267
PFAA	-.009	-.185	.869	.702	.336	.663	.736	1.000	.635	-.250
DO	-.753	-.773	.542	.096	.122	.922	.334	.635	1.000	.405
PPCHO	-.622	-.458	-.296	-.797	.083	-.187	-.267	-.250	.405	1.000

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.9a:- Correlation coefficients of various constituents in particulate matter at Station 1 for diurnal variation

	PP	PT&L	PTCHO	PMCHO	POC	PTL	PHS	PFAA	DO	PPCHO
Temp.	.554	-.941(*)	.083	.626	.563	.520	.703	.782	.902(*)	-.478
pH	.902(*)	-.856	-.067	.314	-.033	.351	.759	.192	.937(*)	-.302
S(‰)	.867	-.253	-.415	-.430	-.228	-.103	.803	-.164	.606	.120
Alk.	.629	-.611	.341	.211	-.217	.499	.351	-.119	.557	.021
Chl.	.339	-.859	.553	.564	.811	.847	.573	.891(*)	.717	-.153
TSS	.109	-.727	.519	.600	.915(*)	.760	.424	.976(**)	.553	-.202
DH	-.136	-.196	.841	.301	.144	.702	-.254	-.053	-.108	.369
PP	1.000	-.634	-.089	-.114	-.087	.288	.891(*)	.027	.857	.044
PT&L	-.634	1.000	-.223	-.638	-.417	-.628	-.665	-.633	-.922(*)	.407
PTCHO	-.089	-.223	1.000	.046	.578	.882(*)	.056	.381	.023	.543
PMCHO	-.114	-.638	.046	1.000	.310	.230	-.100	.575	.351	-.814
POC	-.087	-.417	.578	.310	1.000	.699	.330	.934(*)	.288	.075
PTL	.288	-.628	.882(*)	.230	.699	1.000	.457	.620	.484	.320
PHS	.891(*)	-.665	.056	-.100	.330	.457	1.000	.389	.877	.116
PFAA	.027	-.633	.381	.575	.934(*)	.620	.389	1.000	.487	-.262
DO	.857	-.922(*)	.023	.351	.288	.484	.877	.487	1.000	-.282
PPCHO	.044	.407	.543	-.814	.075	.320	.116	-.262	-.282	1.000

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.9b:- Correlation coefficients of various constituents in particulate matter at Station 2 for diurnal variation

	PP	PT&L	PTCHO	PMCHO	POC	PTL	PHS	PFAA	DO	PPCHO
Temp.	.615	-.830	.105	.079	.087	.065	-.127	-.135	.139	.063
pH	.831	-.619	.826	-.759	.479	.571	.637	-.217	-.693	.926(*)
S(‰)	-.004	.200	.000	-.210	.593	-.342	-.052	.127	-.084	.066
Alk.	.144	-.009	-.183	-.233	.596	-.601	-.343	.336	.187	-.079
Chl.	.254	-.577	-.320	.429	-.122	-.264	-.486	.010	.517	-.401
TSS	.638	-.418	.656	-.461	.946(*)	.222	.471	-.318	-.616	.691
DH	-.874	.836	-.226	.290	.088	-.194	-.009	.004	-.017	-.281
PP	1.000	-.925(*)	.642	-.511	.725	.265	.321	-.230	-.422	.694
PT&L	-.925(*)	1.000	-.473	.179	-.616	-.195	-.158	.317	.228	-.450
PTCHO	.642	-.473	1.000	-.401	.590	.858	.931(*)	-.687	-.963(**)	.958(*)
PMCHO	-.511	.179	-.401	1.000	-.259	-.083	-.250	-.389	.334	-.648
POC	.725	-.616	.590	-.259	1.000	.157	.352	-.406	-.496	.572
PTL	.265	-.195	.858	-.083	.157	1.000	.951(*)	-.788	-.892(*)	.740
PHS	.321	-.158	.931(*)	-.250	.352	.951(*)	1.000	-.740	-.985(**)	.853
PFAA	-.230	.317	-.687	-.389	-.406	-.788	-.740	1.000	.709	-.450
DO	-.422	.228	-.963(**)	.334	-.496	-.892(*)	-.985(**)	.709	1.000	-.906(*)
PPCHO	.694	-.450	.958(*)	-.648	.572	.740	.853	-.450	-.906(*)	1.000

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.9c:- Correlation coefficients of various constituents in particulate matter at Station R for diurnal variation

	STAA	SFAA	SCAA	SMCHO	STCHO	SPCHO	SP	ST&L	STL	SHS	SOC
STAA	1.000	-.118	1.000(**)	-.314	-.539(*)	-.534(*)	.576(*)	-.231	-.111	-.753(**)	-.450
SFAA	-.118	1.000	-.129	.752(**)	.309	.281	.020	.079	.231	.169	.605(*)
SCAA	1.000(**)	-.129	1.000	-.322	-.542(*)	-.536(*)	.575(*)	-.231	-.113	-.754(**)	-.457
SMCHO	-.314	.752(**)	-.322	1.000	.378	.340	-.065	-.065	.007	.160	.566(*)
STCHO	-.539(*)	.309	-.542(*)	.378	1.000	.999(**)	-.391	-.130	.318	.200	.542(*)
SPCHO	-.534(*)	.281	-.536(*)	.340	.999(**)	1.000	-.385	-.140	.595(*)	.118	.537(*)
SP	.576(*)	.020	.575(*)	-.065	-.391	-.385	1.000	-.022	.225	-.567(*)	-.309
ST&L	-.231	.079	-.231	-.065	-.130	-.140	-.022	1.000	-.166	.133	-.191
STL	-.111	.231	-.113	.007	.318	.595(*)	.225	-.166	1.000	-.302	.275
SHS	-.753(**)	.169	-.754(**)	.160	.200	.118	-.567(*)	.133	-.302	1.000	.494
SOC	-.450	.605(*)	-.457	.566(*)	.542(*)	.537(*)	-.309	-.191	.275	.494	1.000
S Cl-	-.169	-.035	-.169	-.005	-.037	-.038	.283	.188	-.050	.077	-.373

Table C.10a:- Correlation coefficients of sedimentary organic constituents at Station 1

	STAA	SFAA	SCAA	SMCHO	STCHO	SPCHO	SP	ST&L	STL	SHS	SOC
STAA	1.000	-.011	1.000(**)	-.427	-.311	-.293	.653(*)	-.287	-.006	-.859(**)	-.277
SFAA	-.011	1.000	-.022	.413	.209	.188	.196	.478	.424	.075	.275
SCAA	1.000(**)	-.022	1.000	-.431	-.314	-.295	.651(*)	-.292	-.011	-.860(**)	-.280
SMCHO	-.427	.413	-.431	1.000	.596(*)	.548(*)	-.059	.153	.144	.179	.277
STCHO	-.311	.209	-.314	.596(*)	1.000	.998(**)	.302	-.172	.590(*)	.189	.634(**)
SPCHO	-.293	.188	-.295	.548(*)	.998(**)	1.000	.322	-.243	.643(*)	.130	.728(**)
SP	.653(*)	.196	.651(*)	-.059	.302	.322	1.000	-.259	.307	-.473	-.010
ST&L	-.287	.478	-.292	.153	-.172	-.243	-.259	1.000	-.188	.452	-.249
STL	-.006	.424	-.011	.144	.590(*)	.643(*)	.307	-.188	1.000	.140	.614(*)
SHS	-.859(**)	.075	-.860(**)	.179	.189	.130	-.473	.452	.140	1.000	.087
SOC	-.277	.275	-.280	.277	.634(**)	.728(**)	-.010	-.249	.614(*)	.087	1.000
S Cl-	-.223	-.105	-.221	.384	.011	-.017	-.396	.067	-.207	.075	-.236

Table C.10b:- Correlation coefficients of sedimentary organic constituents at Station 2

	STAA	SFAA	SCAA	SMCHO	STCHO	SPCHO	SP	ST&L	STL	SHS	SOC
STAA	1.000	.437	1.000(**)	-.056	-.251	-.255	.250	-.219	-.096	-.157	.370
SFAA	.437	1.000	.421	.470	.609(*)	.603(*)	.191	.025	.257	-.118	.600(*)
SCAA	1.000(**)	.421	1.000	-.066	-.265	-.269	.248	-.222	-.103	-.156	.361
SMCHO	-.056	.470	-.066	1.000	.579(*)	.547(*)	.038	-.088	.033	-.052	.093
STCHO	-.251	.609(*)	-.265	.579(*)	1.000	.999(**)	-.198	.388	-.018	.136	-.092
SPCHO	-.255	.603(*)	-.269	.547(*)	.999(**)	1.000	-.036	.401	.226	.014	.186
SP	.250	.191	.248	.038	-.198	-.036	1.000	.117	.716(**)	-.272	.761(**)
ST&L	-.219	.025	-.222	-.088	.388	.401	.117	1.000	.312	.425	.014
STL	-.096	.257	-.103	.033	-.018	.226	.716(**)	.312	1.000	-.204	.643(**)
SHS	-.157	-.118	-.156	-.052	.136	.014	-.272	.425	-.204	1.000	-.480
SOC	.370	.600(*)	.361	.093	-.092	.186	.761(**)	.014	.643(**)	-.480	1.000
S Cl-	.135	-.226	.140	.028	-.422	-.434	.298	-.349	.194	-.104	-.016

Table C.10c:- Correlation coefficients of sedimentary organic constituents at Station 3

	STAA	SFAA	SCAA	SMCHO	STCHO	SPCHO	SP	ST&L	STL	SHS	SOC	SON
STAA	1	0.798	.999(**)	0.487	0.628	0.603	0.134	0.525	0.909	0.82	0.476	0.426
SFAA	0.798	1	0.777	0.915	0.825	0.803	0.406	0.72	0.663	0.884	0.834	-0.055
SCAA	.999(**)	0.777	1	0.458	0.609	0.585	0.118	0.508	0.912	0.806	0.451	0.448
SMCHO	0.487	0.915	0.458	1	0.758	0.741	0.472	0.671	0.34	0.719	0.876	-0.345
TCHO	0.628	0.825	0.609	0.758	1	.999(**)	0.834	.986(*)	0.742	.960(*)	.959(*)	-0.436
SPCHO	0.603	0.803	0.585	0.741	.999(**)	1	0.854	.992(**)	0.733	.951(*)	.958(*)	-0.462
SP	0.134	0.406	0.118	0.472	0.834	0.854	1	0.91	0.418	0.666	0.827	-0.803
ST&L	0.525	0.72	0.508	0.671	.986(*)	.992(**)	0.91	1	0.704	0.915	0.939	-0.534
STL	0.909	0.663	0.912	0.34	0.742	0.733	0.418	0.704	1	0.878	0.538	0.203
SHS	0.82	0.884	0.806	0.719	.960(*)	.951(*)	0.666	0.915	0.878	1	0.872	-0.168
SOC	0.476	0.834	0.451	0.876	.959(*)	.958(*)	0.827	0.939	0.538	0.872	1	-0.573
SON	0.426	-0.055	0.448	-0.345	-0.436	-0.462	-0.803	-0.534	0.203	-0.168	-0.573	1
S Cl-	0.75	.956(*)	0.73	0.874	.955(*)	0.943	0.647	0.892	0.739	.966(*)	0.937	-0.252
Sand	-0.86	-0.59	-0.871	-0.277	-0.925	-0.939	-0.938	-0.98	-0.99	-0.911	-0.759	-0.657
Clay	0.562	0.191	0.58	-0.157	0.676	0.703	0.996	0.804	0.835	0.649	0.41	0.275
Silt	0.941	0.731	0.947	0.452	0.98	0.987	0.856	1.000(**)	.999(*)	0.972	0.867	0.787

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.11a:- Correlation coefficients of sedimentary organic constituents during premonsoon

	STAA	SFAA	SCAA	SMCHO	TCHO	SPCHO	SP	ST&L	STL	SHS	SOC	SON
STAA	1	1.000(**)	1.000(**)	.999(**)	0.949	0.938	.991(**)	.989(*)	.998(**)	1.000(**)	1.000(**)	.984(*)
SFAA	1.000(**)	1	1.000(**)	1.000(**)	0.94	0.929	.994(**)	.984(*)	.999(**)	1.000(**)	.999(**)	.988(*)
SCAA	1.000(**)	1.000(**)	1	.999(**)	0.949	0.939	.991(**)	.989(*)	.997(**)	1.000(**)	1.000(**)	.984(*)
SMCHO	.999(**)	1.000(**)	.999(**)	1	0.932	0.92	.996(**)	.980(*)	1.000(**)	1.000(**)	.997(**)	.992(**)
TCHO	0.949	0.94	0.949	0.932	1	1.000(**)	0.897	.986(*)	0.924	0.939	.957(*)	0.877
SPCHO	0.938	0.929	0.939	0.92	1.000(**)	1	0.883	.980(*)	0.912	0.927	0.947	0.862
SP	.991(**)	.994(**)	.991(**)	.996(**)	0.897	0.883	1	.959(*)	.998(**)	.994(**)	.987(*)	.999(**)
ST&L	.989(*)	.984(*)	.989(*)	.980(*)	.986(*)	.980(*)	.959(*)	1	.976(*)	.984(*)	.992(**)	0.946
STL	.998(**)	.999(**)	.997(**)	1.000(**)	0.924	0.912	.998(**)	.976(*)	1	.999(**)	.995(**)	.994(**)
SHS	1.000(**)	1.000(**)	1.000(**)	1.000(**)	0.939	0.927	.994(**)	.984(*)	.999(**)	1	.998(**)	.989(*)
SOC	1.000(**)	.999(**)	1.000(**)	.997(**)	.957(*)	0.947	.987(*)	.992(**)	.995(**)	.998(**)	1	.979(*)
SON	.984(*)	.988(*)	.984(*)	.992(**)	0.877	0.862	.999(**)	0.946	.994(**)	.989(*)	.979(*)	1
S Cl-	.996(**)	.998(**)	.996(**)	.999(**)	0.918	0.905	.999(**)	.972(*)	1.000(**)	.998(**)	.994(**)	.996(**)
Sand	-0.972	-0.964	-0.973	-0.957	-0.988	-0.981	-0.922	-.999(*)	-0.949	-0.963	-0.979	-0.902
Clay	0.922	0.909	0.922	0.897	1.000(**)	1.000(*)	0.847	0.977	0.886	0.907	0.934	0.82
Silt	0.989	0.984	0.989	0.979	0.97	0.96	0.953	.999(*)	0.973	0.983	0.993	0.937

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.11b:- Correlation coefficients of sedimentary organic constituents during monsoon

	STAA	SFAA	SCAA	SMCHO	TCHO	SPCHO	SP	ST&L	STL	SHS	SOC	SON
STAA	1	0.891	1.000(**)	0.916	.952(*)	0.943	.997(**)	.959(*)	.996(**)	0.782	.963(*)	.980(*)
SFAA	0.891	1	0.888	.998(**)	0.709	0.689	0.923	0.727	0.929	.980(*)	.980(*)	.964(*)
SCAA	1.000(**)	0.888	1	0.913	.954(*)	0.945	.997(**)	.961(*)	.995(**)	0.777	.961(*)	.979(*)
SMCHO	0.916	.998(**)	0.913	1	0.749	0.73	0.944	0.766	0.949	.966(*)	.990(**)	.978(*)
TCHO	.952(*)	0.709	.954(*)	0.749	1	1.000(**)	0.926	1.000(**)	0.919	0.553	0.834	0.872
SPCHO	0.943	0.689	0.945	0.73	1.000(**)	1	0.915	.999(**)	0.908	0.529	0.818	0.857
SP	.997(**)	0.923	.997(**)	0.944	0.926	0.915	1	0.935	1.000(**)	0.826	.981(*)	.992(**)
ST&L	.959(*)	0.727	.961(*)	0.766	1.000(**)	.999(**)	0.935	1	0.929	0.574	0.848	0.884
STL	.996(**)	0.929	.995(**)	0.949	0.919	0.908	1.000(**)	0.929	1	0.836	.984(*)	.994(**)
SHS	0.782	.980(*)	0.777	.966(*)	0.553	0.529	0.826	0.574	0.536	1	0.921	0.89
SOC	.963(*)	.980(*)	.961(*)	.990(**)	0.834	0.818	.981(*)	0.848	.984(*)	0.921	1	.997(**)
SON	.980(*)	.964(*)	.979(*)	.978(*)	0.872	0.857	.992(**)	0.884	.994(**)	0.89	.997(**)	1
S Cl-	.998(**)	0.862	.999(**)	0.891	.969(*)	.961(*)	.991(**)	.975(*)	.988(*)	0.743	0.945	.966(*)
Sand	-0.906	-0.547	-0.91	-0.601	-.998(*)	-1.000(*)	-0.863	-0.996	-0.852	-0.357	-0.72	-0.778
Clay	0.579	0.063	0.586	0.128	0.838	0.856	0.502	0.822	0.483	-0.15	0.284	0.366
Silt	0.959	0.667	0.962	0.715	0.996	0.992	0.929	.998(*)	0.922	0.494	0.817	0.863

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.11c:- Correlation coefficients of sedimentary organic constituents during postmonsoon

	Depth	SOC	SON	Sand	Clay	Silt	Silt+Clay
SOC	0-2	1	0.86261**	-0.9803**	0.99546**	0.92938**	0.97939**
	2--4	1	0.9144**	-0.8948**	0.86924**	0.90306**	0.8947**
	4--6	1	0.91142**	-0.9613**	0.97327**	0.9481**	0.95814**
	6--10	1	0.95577**				
	10--20	1	0.94105**	-0.7579**	0.972**	0.58586	0.76686**
	20-30	1	0.98803**				
SON	0-2	0.86261**	1	-0.8447**	0.96361**	0.73579**	0.8423**
	2--4	0.9144**	1	-0.8254**	0.79356**	0.83593**	0.8253**
	4--6	0.91142**	1	-0.8452**	0.86947**	0.82047**	0.83903**
	6--10	0.95577**	1				
	10--20	0.94105**	1	-0.6898*	0.94403**	0.50292	0.6997**
	20-30	0.98803**	1				
C/N	0-2	0.14119	-0.3659	0.39046	-0.6407*	-0.2202	-0.3864
	2--4	-0.2891	-0.5949	0.74482**	-0.7075*	-0.7573**	-0.7447**
	4--6	-0.4361	-0.7435**	0.82363**	-0.8495**	-0.7975**	-0.8171**
	6--10	-0.6782*	-0.8269**				
	10--20	0.05189	-0.2774	0.52625	-0.8561**	-0.3145	-0.5379
	20-30	-0.1413	-0.271				
SFAA	0-2	0.53029	0.52403	-0.6668*	0.85427**	0.52334	0.6635*
	2--4	0.67596*	0.63134*	-0.9483**	0.92972**	0.95416**	0.94827**
	4--6	0.74035*	0.59421	-0.8688**	0.89124**	0.84587**	0.86313**
	6--10	0.62668*	0.50344	-0.9261**	0.77245**	0.98234**	0.92505**
	10--20	0.87317**	0.7458**	-0.7912**	0.98302**	0.6277*	0.79958**
	20-30	0.87038**	0.85648**				
SCAA	0-2	0.38461	0.60535*	-0.7845**	0.93062**	0.66143*	0.78173**
	2--4	0.45859	0.68889*	-0.6963*	0.6563*	0.70971*	0.69614*
	4--6	0.67677*	0.83825**	-0.9746**	0.98407**	0.96361**	0.97197**
	6--10	0.66261*	0.81955**	-0.8647**	0.67662*	0.94678**	0.86323**
	10--20	0.67377*	0.72208*	-0.9594**	0.72527**	0.99866**	0.95542**
	20-30	0.82739**	0.81094**				
STAA	0-2	0.40927	0.63029*	-0.7819**	0.92909**	0.6583*	0.77913**
	2--4	0.47642	0.70461*	-0.6992*	0.65933*	0.71254*	0.69902*
	4--6	0.69857*	0.85294**	-0.9736**	0.98326**	0.96239**	0.97089**
	6--10	0.67668*	0.8304**	-0.8655**	0.67781*	0.94729**	0.86404**
	10--20	0.68776*	0.73166*	-0.9602**	0.72712*	0.9988**	0.95621**
	20-30	0.83284**	0.81644**				
SP	0-2	0.62293*	0.78688**	-0.7687**	0.92118**	0.64248*	0.7659**
	2--4	0.86011**	0.76966**	-0.9971**	0.99154**	0.99838**	0.99711**
	4--6	0.76392**	0.75232**	-0.9589**	0.94438**	0.97057**	0.96203**
	6--10	0.80474**	0.79002**				
	10--20	0.48697	0.71274*	-0.9128**	0.99861**	0.79312**	0.91836**
	20-30	0.83665**	0.89971**				

Table C.12a:- Downcore correlation coefficients of various constituents with organic carbon, organic nitrogen and sediment texture

	Depth	SOC	SON	Sand	Clay	Silt	Silt+Clay
SMCHO	0-2	0.55702	0.73988**	-0.6033*	0.80864**	0.45152	0.59974
	2--4	0.6804*	0.67041	-0.9183**	0.93845**	0.91068**	0.9184**
	4--6	0.62382*	0.68069*	-0.6906*	0.724*	0.65765*	0.68233*
	6--10	0.63653*	0.66359*				
	10--20	0.53544	0.55382	-0.8058**	0.44714	0.92122**	0.79755**
	20-30	0.35121	0.45221				
STCHO	0-2	0.863**	0.94884**	-0.9623**	0.99982**	0.89848**	0.96111**
	2--4	0.95739**	0.83379**	-0.8717**	0.84379**	0.88078**	0.87158**
	4--6	0.92089**	0.97576**	-0.9537**	0.96683**	0.93931**	0.95019**
	6--10	0.84616**	0.76242**				
	10--20	0.96776**	0.9221**	-0.5849	0.89037**	0.38065	0.59599
	20-30	0.97298**	0.97899**				
SPCHO	0-2	0.86926**	0.94846**	-0.9705**	0.99872**	0.91194**	0.96938**
	2--4	0.9498**	0.82365**	-0.8564**	0.82705**	0.86594**	0.85623**
	4--6	0.92309**	0.97675**	-0.959**	0.97132**	0.9454**	0.95571**
	6--10	0.81105**	0.72419*				
	10--20	0.96863**	0.92049**	-0.5562	0.87395**	0.34816	0.56762
	20-30	0.97794**	0.98049**				
STL	0-2	0.72934*	0.53277	-0.6446*	0.39516	0.7705**	0.64796*
	2--4	0.84717**	0.68541*	-0.8281**	0.7964**	0.83849**	0.82794**
	4--6	0.91048**	0.79629**	-0.6448*	0.68018*	0.61004*	0.63605*
	6--10	0.79545**	0.711*				
	10--20	0.74662**	0.78104**	-0.3405	0.73175*	0.11299	0.35343
	20-30	0.99705**	0.99404**				
ST&L	0-2	0.64585*	0.43304	-0.8628**	0.67917*	0.9391**	0.86507**
	2--4	0.61014*	0.43261	-0.3903	0.43968	0.37282	0.39047
	4--6	0.60882*	0.59103	-0.9633**	0.94958**	0.97434**	0.96632**
	6--10	0.57072	0.49531				
	10--20	0.50019	0.42937	-0.742**	0.35473	0.87734**	0.7327
	20-30	0.61492*	0.63145*				
SHA	0-2	0.4113	0.52396	-0.9722**	0.99833**	0.91486**	0.97112**
	2--4	0.72059*	0.76091**	-0.6813*	0.64057*	0.69501*	0.68115*
	4--6	0.66855*	0.77239**	-0.8519**	0.87571**	0.82771**	0.84591**
	6--10	0.71799*	0.73564**				
	10--20	0.68907*	0.79564**	-0.9361**	0.99352**	0.82887**	0.94083**
	20-30	0.78159**	0.71141*				

Table C.12b:- Downcore correlation coefficients of various constituents with organic carbon, organic nitrogen and sediment texture

		0-2	2—4	4--6	6--10	10--20	20-30
SOC	0-2	1					
	2--4	0.98177**	1				
	4--6	0.9877**	0.9696**	1			
	6--10	0.9538**	0.95736**	0.97734**	1		
	10--20	0.92479**	0.95194**	0.93667**	0.89658**	1	
	20-30	0.83539**	0.85524**	0.85349**	0.72095*	0.96595**	1
SON	0-2	1					
	2--4	0.9864**	1				
	4--6	0.96389**	0.97878**	1			
	6--10	0.9949**	0.99062**	0.98114**	1		
	10--20	0.87134**	0.92765**	0.94522**	0.88355**	1	
	20-30	0.69083*	0.71997*	0.71417*	0.63791*	0.83195**	1
C/N	0-2	1					
	2--4	0.80711**	1				
	4--6	0.73822**	0.84389**	1			
	6--10	0.58299	0.52794	0.63627*	1		
	10--20	0.57493	0.36251	0.59221	0.5494	1	
	20-30	0.24399	0.56948	0.08596	0.39513	-0.0754	1
STAA	0-2	1					
	2--4	0.92601**	1				
	4--6	0.85893**	0.75618**	1			
	6--10	0.90651**	0.89348**	0.86038**	1		
	10--20	0.4224	0.27578	0.8089**	0.5132	1	
	20-30	0.85553**	0.85644**	0.96302**	0.88707**	0.87077**	1
SFAA	0-2	1					
	2--4	0.94392**	1				
	4--6	0.89624**	0.94308**	1			
	6--10	0.90158**	0.91169**	0.98258**	1		
	10--20	0.50329	0.68579*	0.76689**	0.71714*	1	
	20-30	0.41475	0.34698	0.50814	0.65711*	0.7255*	1
SCAA	0-2	1					
	2--4	0.91996**	1				
	4--6	0.86161**	0.75502**	1			
	6--10	0.8999**	0.8895**	0.85807**	1		
	10--20	0.4204	0.26937	0.80357**	0.50509	1	
	20-30	0.85769**	0.85895**	0.96319**	0.88689**	0.87682**	1
SP	0-2	1					
	2--4	0.75745**	1				
	4--6	0.71614	0.8201**	1			
	6--10	0.83762**	0.8365**	0.89428**	1		
	10--20	0.74307**	0.63879	0.88627**	0.85844**	1	
	20-30	0.49495	0.70459	0.78695**	0.56392	0.47461	1

Table C.13a:- Correlation matrix of various organic constituents between depths

		0-2	2—4	4—6	6—10	10--20	20-30
SMCHO	0-2	1					
	2--4	0.60984*	1				
	4--6	0.92652**	0.60221	1			
	6--10	0.81918**	0.69822	0.87397**	1		
	10--20	0.47348	0.393	0.69495*	0.6845*	1	
	20-30	0.38696	0.65838*	0.72847*	0.67427*	0.94079**	1
STCHO	0-2	1					
	2--4	0.84604**	1				
	4--6	0.94621**	0.86029**	1			
	6--10	0.74953**	0.87719**	0.78329**	1		
	10--20	0.73109*	0.90926**	0.81827**	0.89557**	1	
	20-30	0.67401*	0.88437**	0.69697*	0.98139**	0.89669**	1
SPCHO	0-2	1					
	2--4	0.83893**	1				
	4--6	0.93875**	0.84976**	1			
	6--10	0.72948*	0.86478**	0.76331**	1		
	10--20	0.72597*	0.89924**	0.81855**	0.87782**	1	
	20-30	0.68916*	0.89318**	0.70908*	0.98736**	0.89182**	1
STL	0-2	1					
	2--4	0.78654**	1				
	4--6	0.79254**	0.92373**	1			
	6--10	0.79126**	0.89296**	0.98839**	1		
	10--20	0.73122*	0.83829**	0.96909**	0.96137**	1	
	20-30	0.68343*	0.72623*	0.8696**	0.82143**	0.88783**	1
ST&L	0-2	1					
	2--4	0.93565**	1				
	4--6	0.8869**	0.77415**	1			
	6--10	0.82006**	0.79997**	0.92493**	1		
	10--20	0.82252**	0.76638**	0.8511**	0.87853**	1	
	20-30	0.86185**	0.90922**	0.65635*	0.84174**	0.97299**	1
SHA	0-2	1					
	2--4	0.88523**	1				
	4--6	0.94402**	0.93509**	1			
	6--10	0.96118**	0.90962**	0.96795**	1		
	10--20	0.94231**	0.73394	0.90556**	0.89561**	1	
	20-30	0.90201**	0.90877**	0.93821**	0.8914**	0.98455**	1

Table C.13b:- Correlation matrix of various organic constituents between depths

	SNa	SK	SCa	SFe	SMg	SMn	SNi	SCu	SZn	SCo	SPb	SCr
SNa	1.000	.695(**)	-.473	.519	.388	-.568(*)	-.529	-.444	-.337	-.426	-.487	-.544
SK	.695(**)	1.000	-.978(**)	.897(**)	.856(**)	-.451	-.740(**)	-.379	-.181	-.124	-.558(*)	-.613(*)
SCa	-.473	-.978(**)	1.000	-.786(*)	-.724(*)	.579	.973(**)	.431	-.196	-.087	.933(**)	.955(**)
SFe	.519	.897(**)	-.786(*)	1.000	.915(**)	-.261	-.624(**)	-.267	-.139	-.022	-.407	-.450
SMg	.388	.856(**)	-.724(*)	.915(**)	1.000	-.320	-.635(**)	-.156	-.026	.217	-.462	-.497
SMn	-.568(*)	-.451	.579	-.261	-.320	1.000	.796(**)	.767(**)	.453	.510(*)	.755(**)	.818(**)
SNi	-.529	-.740(**)	.973(**)	-.624(**)	-.635(**)	.796(**)	1.000	.767(**)	.428	.403	.776(**)	.933(**)
SCu	-.444	-.379	.431	-.267	-.156	.767(**)	.767(**)	1.000	.581(*)	.839(**)	.639(**)	.742(**)
SZn	-.337	-.181	-.196	-.139	-.026	.453	.428	.581(*)	1.000	.616(*)	.181	.391
SCo	-.426	-.124	-.087	-.022	.217	.510(*)	.403	.839(**)	.616(*)	1.000	.397	.356
SPb	-.487	-.558(*)	.933(**)	-.407	-.462	.755(**)	.776(**)	.639(**)	.181	.397	1.000	.652(**)
SCr	-.544	-.613(*)	.955(**)	-.450	-.497	.818(**)	.933(**)	.742(**)	.391	.356	.652(**)	1.000

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.14a:- Correlation Coefficients of Metals in mangrove surface sediments at Station 1

	SNa	SK	SCa	SFe	SMg	SMn	SNi	SCu	SZn	SCo	SPb	SCr
SNa	1.000	.724(**)	-.560	.645(*)	.656(*)	-.534	-.601(*)	-.524	-.454	-.480	-.311	-.567(*)
SK	.724(**)	1.000	-.727(*)	.941(**)	.929(**)	-.502	-.676(**)	-.276	-.418	-.148	-.392	-.598(*)
SCa	-.560	-.727(*)	1.000	-.647	-.664	-.022	.664	-.079	-.033	-.370	.435	.315
SFe	.645(*)	.941(**)	-.647	1.000	.971(**)	-.356	-.610(*)	-.167	-.378	.039	-.348	-.449
SMg	.656(*)	.929(**)	-.664	.971(**)	1.000	-.431	-.663(**)	-.160	-.403	.098	-.395	-.496
SMn	-.534	-.502	-.022	-.356	-.431	1.000	.902(**)	.691(**)	.671(**)	.536(*)	.776(**)	.917(**)
SNi	-.601(*)	-.676(**)	.664	-.610(*)	-.663(**)	.902(**)	1.000	.687(**)	.662(**)	.416	.794(**)	.931(**)
SCu	-.524	-.276	-.079	-.167	-.160	.691(**)	.687(**)	1.000	.495	.827(**)	.721(**)	.762(**)
SZn	-.454	-.418	-.033	-.378	-.403	.671(**)	.662(**)	.495	1.000	.474	.306	.681(**)
SCo	-.480	-.148	-.370	.039	.098	.536(*)	.416	.827(**)	.474	1.000	.365	.592(*)
SPb	-.311	-.392	.435	-.348	-.395	.776(**)	.794(**)	.721(**)	.306	.365	1.000	.711(**)
SCr	-.567(*)	-.598(*)	.315	-.449	-.496	.917(**)	.931(**)	.762(**)	.681(**)	.592(*)	.711(**)	1.000

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.14b:- Correlation Coefficients of Metals in mangrove surface sediments at Station 2

	Sna	SK	SCa	SFe	SMg	SMn	SNi	SCu	SZn	SCo	SPb	SCr
SNa	1.000	-.191	.801(*)	-.126	-.271	-.203	-.230	-.319	-.315	-.028	-.220	.034
SK	-.191	1.000	.862(**)	.919(**)	.480	-.140	-.601(*)	-.447	-.370	-.651(*)	-.555(*)	.565(*)
SCa	.801(*)	.862(**)	1.000	.907(**)	-.398	.679	.250	.473	.424	.158	.215	1.000(**)
SFe	-.126	.919(**)	.907(**)	1.000	.496	.021	-.522(*)	-.354	-.263	-.553(*)	-.481	.643(**)
SMg	-.271	.480	-.398	.496	1.000	-.462	-.587(*)	-.398	-.250	-.489	-.546(*)	-.252
SMn	-.203	-.140	.679	.021	-.462	1.000	.859(**)	.702(**)	.899(**)	.868(**)	.828(**)	.427
SNi	-.230	-.601(*)	.250	-.522(*)	-.587(*)	.859(**)	1.000	.787(**)	.616(*)	.850(**)	.988(**)	.888(**)
SCu	-.319	-.447	.473	-.354	-.398	.702(**)	.787(**)	1.000	.580(*)	.672(**)	.784(**)	.769(**)
SZn	-.315	-.370	.424	-.263	-.250	.899(**)	.616(*)	.580(*)	1.000	.768(**)	.575(*)	.852(**)
SCo	-.028	-.651(*)	.158	-.553(*)	-.489	.868(**)	.850(**)	.672(**)	.768(**)	1.000	.835(**)	.805(**)
SPb	-.220	-.555(*)	.215	-.481	-.546(*)	.828(**)	.988(**)	.784(**)	.575(*)	.835(**)	1.000	.848(**)
SCr	.034	.565(*)	1.000(**)	.643(**)	-.252	.427	.888(**)	.769(**)	.852(**)	.805(**)	.848(**)	1.000

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.14c:- Correlation Coefficients of Metals in mangrove surface sediments at Station 3

	SNa	SK	SCa	SFe	SMg	SMn	SNi	SCu	SZn	SCo	SPb	SCr
SOC	0.878	0.889	.970(*)	0.599	0.799	0.769	0.941	0.803	0.756	.964(*)	-0.751	0.912
SON	-0.111	-0.22	-0.366	0.114	0	0.083	-0.657	-0.317	0	-0.704	.964(*)	-0.462
S Cl-	.989(*)	.965(*)	.992(**)	0.774	.950(*)	0.943	0.841	0.831	0.88	0.845	-0.473	0.893
SNa	1	.952(*)	.964(*)	0.798	.971(*)	.981(*)	0.76	0.792	0.914	0.759	-0.346	0.839
SK	.952(*)	1	.964(*)	0.897	.972(*)	0.908	0.875	0.941	0.747	0.847	-0.405	.954(*)
SCa	.964(*)	.964(*)	1	0.748	0.92	0.895	0.899	0.856	0.833	0.904	-0.57	0.928
SFe	0.798	0.897	0.748	1	0.918	0.814	0.66	0.905	0.528	0.583	-0.023	0.819
SMg	.971(*)	.972(*)	0.92	0.918	1	.971(*)	0.739	0.865	0.815	0.709	-0.211	0.859
SMn	.981(*)	0.908	0.895	0.814	.971(*)	1	0.63	0.725	0.922	0.621	-0.161	0.746
SNi	0.76	0.875	0.899	0.66	0.739	0.63	1	0.905	0.517	.992(**)	-0.766	.971(*)
SCu	0.792	0.941	0.856	0.905	0.865	0.725	0.905	1	0.479	0.85	-0.427	.975(*)
SZn	0.914	0.747	0.833	0.528	0.815	0.922	0.517	0.479	1	0.557	-0.265	0.573
SCo	0.759	0.847	0.904	0.583	0.709	0.621	.992(**)	0.85	0.557	1	-0.824	0.943
SPb	-0.346	-0.405	-0.57	-0.023	-0.211	-0.161	-0.766	-0.427	-0.265	-0.824	1	-0.593
SCr	0.839	.954(*)	0.928	0.819	0.859	0.746	.971(*)	.975(*)	0.573	0.943	-0.593	1
Sand	-0.747	-0.922	-0.799	-0.992	-0.873	-0.733	-0.989	-1.000(**)	-0.409	-0.951	-0.884	-0.987
Clay	0.395	0.67	0.468	0.843	0.584	0.375	0.833	0.901	-0.017	0.73	.999(*)	0.826
Silt	0.859	0.978	0.898	.998(*)	0.949	0.848	.999(*)	0.984	0.573	0.992	0.78	1.000(*)

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.15a:- Correlation Coefficients of Metals in mangrove surface sediments during premonsoon

	SNa	SK	SCa	SFe	SMg	SMn	SNi	SCu	SZn	SCo	SPb	SCr
SOC	-.956(*)	.996(**)	-0.538	.999(**)	.990(*)	.998(**)	1.000(**)	.976(*)	.964(*)	.998(**)	0.908	.992(**)
SON	-0.876	.956(*)	-0.355	.970(*)	.998(**)	.963(*)	.983(*)	1.000(**)	.998(**)	.964(*)	0.803	0.946
S Cl-	-0.916	.979(*)	-0.44	.988(*)	1.000(**)	.983(*)	.996(**)	.995(**)	.988(*)	.985(*)	0.855	.972(*)
SNa	1	-.979(*)	0.762	-.967(*)	-0.904	-.974(*)	-0.95	-0.87	-0.843	-.972(*)	-.991(**)	-.985(*)
SK	-.979(*)	1	-0.615	.999(**)	.972(*)	1.000(**)	.994(**)	.952(*)	0.935	1.000(**)	0.943	1.000(**)
SCa	0.762	-0.615	1	-0.573	-0.412	-0.595	-0.522	-0.344	-0.295	-0.59	-0.842	-0.639
SFe	-.967(*)	.999(**)	-0.573	1	.983(*)	1.000(**)	.998(**)	.967(*)	.952(*)	1.000(**)	0.924	.997(**)
SMg	-0.904	.972(*)	-0.412	.983(*)	1	.977(*)	.992(**)	.997(**)	.992(**)	.979(*)	0.838	.964(*)
SMn	-.974(*)	1.000(**)	-0.595	1.000(**)	.977(*)	1	.996(**)	.959(*)	0.943	1.000(**)	0.935	.998(**)
SNi	-0.95	.994(**)	-0.522	.998(**)	.992(**)	.996(**)	1	.980(*)	.969(*)	.997(**)	0.9	.990(*)
SCu	-0.87	.952(*)	-0.344	.967(*)	.997(**)	.959(*)	.980(*)	1	.999(**)	.961(*)	0.796	0.942
SZn	-0.843	0.935	-0.295	.952(*)	.992(**)	0.943	.969(*)	.999(**)	1	0.946	0.764	0.924
SCo	-.972(*)	1.000(**)	-0.59	1.000(**)	.979(*)	1.000(**)	.997(**)	.961(*)	0.946	1	0.932	.998(**)
SPb	-.991(**)	0.943	-0.842	0.924	0.838	0.935	0.9	0.796	0.764	0.932	1	.953(*)
SCr	-.985(*)	1.000(**)	-0.639	.997(**)	.964(*)	.998(**)	.990(*)	0.942	0.924	.998(**)	.953(*)	1
Sand	0.987	-0.996	0.596	-0.988	-0.93	-0.993	-0.974	-0.896	-0.868	-0.992	-0.949	-.999(*)
Clay	-1.000(**)	0.968	-0.718	0.95	0.858	0.96	0.925	0.812	0.776	0.958	0.987	0.977
Silt	-0.969	1.000(**)	-0.523	.998(*)	0.959	1.000(*)	0.99	0.932	0.909	.999(*)	0.917	.999(*)

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.15b:- Correlation Coefficients of Metals in mangrove surface sediments during monsoon

	SNa	SK	SCa	SFe	SMg	SMn	SNi	SCu	SZn	SCo	SPb	SCr
SOC	.980(*)	.957(*)	0.871	.977(*)	.983(*)	.997(**)	.963(*)	.974(*)	.996(**)	.956(*)	.996(**)	.978(*)
SON	.992(**)	.976(*)	0.833	.990(**)	.994(**)	.989(*)	.980(*)	.988(*)	1.000(**)	.974(*)	.987(*)	.991(**)
S Cl-	.991(**)	.999(**)	0.663	.993(**)	.989(*)	0.918	.998(**)	.995(**)	.970(*)	.999(**)	0.912	.992(**)
SNa	1	.996(**)	0.755	1.000(**)	1.000(**)	.962(*)	.997(**)	1.000(**)	.993(**)	.995(**)	.958(*)	1.000(**)
SK	.996(**)	1	0.691	.997(**)	.994(**)	0.933	1.000(**)	.998(**)	.979(*)	1.000(**)	0.927	.996(**)
SCa	0.755	0.691	1	0.748	0.766	0.906	0.706	0.736	0.825	0.688	0.912	0.751
SFe	1.000(**)	.997(**)	0.748	1	1.000(**)	.959(*)	.998(**)	1.000(**)	.992(**)	.996(**)	.955(*)	1.000(**)
SMg	1.000(**)	.994(**)	0.766	1.000(**)	1	.966(*)	.996(**)	.999(**)	.995(**)	.993(**)	.963(*)	1.000(**)
SMn	.962(*)	0.933	0.906	.959(*)	.966(*)	1	0.94	.954(*)	.987(*)	0.931	1.000(**)	.960(*)
SNi	.997(**)	1.000(**)	0.706	.998(**)	.996(**)	0.94	1	.999(**)	.983(*)	1.000(**)	0.935	.998(**)
SCu	1.000(**)	.998(**)	0.736	1.000(**)	.999(**)	.954(*)	.999(**)	1	.990(*)	.998(**)	0.949	1.000(**)
SZn	.993(**)	.979(*)	0.825	.992(**)	.995(**)	.987(*)	.983(*)	.990(*)	1	.978(*)	.984(*)	.993(**)
SCo	.995(**)	1.000(**)	0.688	.996(**)	.993(**)	0.931	1.000(**)	.998(**)	.978(*)	1	0.925	.996(**)
SPb	.958(*)	0.927	0.912	.955(*)	.963(*)	1.000(**)	0.935	0.949	.984(*)	0.925	1	.956(*)
SCr	1.000(**)	.996(**)	0.751	1.000(**)	1.000(**)	.960(*)	.998(**)	1.000(**)	.993(**)	.996(**)	.956(*)	1
Sand	-0.866	-0.917	-0.251	-0.872	-0.855	-0.657	-0.906	-0.883	-0.789	-0.919	-0.645	-0.87
Clay	0.507	0.6	-0.26	0.517	0.488	0.2	0.58	0.536	0.382	0.605	0.183	0.513
Silt	0.932	0.966	0.394	0.936	0.924	0.763	0.96	0.943	0.872	0.968	0.753	0.934

*Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

Table C.15c:- Correlation Coefficients of Metals in mangrove surface sediments during postmonsoon

	Depth	SOC	SON	Sand	Clay	Silt	Silt+Clay
Na	0-2	0.13198	0.37976	-0.9646**	0.99963**	0.90213**	0.9634**
	2--4	0.24288	0.44545	-0.9762**	0.96301**	0.98014**	0.97617**
	4--6	0.28648	0.52239	-0.9508**	0.96439**	0.93605**	0.94723**
	6--10	0.37339	0.49595	-0.9952**	0.92151**	0.9949**	0.99497**
	10--20	0.50144	0.64727*	-0.4622	0.81566**	0.24374	0.47435
	20-30	0.34417	0.2264				
K	0-2	-0.0192	0.08199	-0.7138*	0.48003	0.82718**	0.7169*
	2--4	0.19606	0.29225	-0.8786**	0.90322**	0.86941**	0.87869**
	4--6	0.25253	0.33019	-0.9288**	0.91021**	0.94438**	0.93292**
	6--10	0.3257	0.35048	-0.9987**	0.96889**	0.96896**	0.99883**
	10--20	0.37058	0.43275	-0.9862**	0.80211**	0.99771**	0.98379**
	20-30	0.254	0.13356				
Ca	0-2	0.848**	0.97429**	-0.8597**	0.97087**	0.75488**	0.85739**
	2--4	0.94944**	0.90531**	-0.9984**	0.99393**	0.99931**	0.99842**
	4--6	0.91799**	0.95288**	-0.9923**	0.99707**	0.98584**	0.99087**
	6--10	0.88656**	0.91089**				
	10--20	0.48608	0.66067*				
	20-30	0.36969	0.44044				
Mg	0-2	0.05258	0.22756	-0.8991**	0.98742**	0.80673**	0.89717**
	2--4	0.20169	0.30084	-0.9911**	0.98236**	0.99341**	0.99104**
	4--6	0.15756	0.32078	-0.9749**	0.98433**	0.964**	0.97231**
	6--10	0.19407	0.27243	-0.9976**	0.97315**	0.96439**	0.99781**
	10--20	0.42503	0.4094	-0.944**	0.99062**	0.84159**	0.94842**
	20-30	0.18284	0.06623				

Table C.16a:- Downcore correlation coefficients of major elements with organic carbon, organic nitrogen and sediment texture

	Depth	SOC	SON	Sand	Clay	Silt	Silt+Clay
Fe	0-2	0.41585	0.63028*	-0.8487**	0.65886*	0.92936**	0.85104**
	2--4	0.39275	0.55996	-0.9106**	0.88681**	0.91823**	0.9105**
	4--6	0.67849*	0.83449**	-0.772**	0.80114**	0.74284**	0.76469**
	6--10	0.49735	0.54274	-0.9933**	0.91431**	0.99656**	0.99299**
	10--20	0.42619	0.56147	-0.9552**	0.98507**	0.86044**	0.95919**
	20-30	0.97721**	0.98997**				
Mn	0-2	0.743**	0.89707**	-0.7936**	0.93593**	0.67246	0.79087**
	2--4	0.79781**	0.91912**	-0.9201**	0.8975**	0.92735**	0.92004**
	4--6	0.76209**	0.92696**	-0.954**	0.96707**	0.93963**	0.95049**
	6--10	0.77171**	0.87579**	-0.9568**	0.82749**	0.99537**	0.95601**
	10--20	0.75392**	0.90102**	-0.7305*	0.96153**	0.55207	0.73985**
	20-30	0.8995**	0.84848**				
Ni	0-2	0.87104**	0.84693**	-0.909**	0.99081**	0.82018**	0.90714**
	2--4	0.56094	0.61718*	-0.996**	0.99939**	0.99417**	0.99604**

	Depth	SOC	SON	Sand	Clay	Silt	Silt+Clay
	4--6	0.77246**	0.77635**	-0.9997**	0.99972**	0.99768**	0.99939**
	6--10	0.57682	0.53656	-0.9988**	0.9684**	0.96944**	0.99892**
	10--20	0.46866	0.5976	-0.9212**	0.99728**	0.80575**	0.92647**
	20-30	0.82469**	0.881**				
Cu	0-2	0.70639*	0.7204*	-0.9789**	0.99607**	0.92691**	0.97803**
	2--4	0.39287	0.55996	-0.9592**	0.97312**	0.95367**	0.95924**
	4--6	0.63448*	0.63264*	-0.9369**	0.91931**	0.95154**	0.94079**
	6--10	0.56963	0.56117	-0.9635**	0.99954**	0.89179**	0.96428**
	10--20	0.61614*	0.76766**	-0.9529**	0.98635**	0.85657**	0.95703**
	20-30	0.95506**	0.91881**				
Zn	0-2	0.64776*	0.52804	-0.7235*	0.89262**	0.58895	0.72046*
	2--4	0.41222	0.66394*	-0.5057	0.45813	0.52191	0.50553
	4--6	0.81425**	0.69986*	-0.9981**	0.9999**	0.99435**	0.99733**
	6--10	0.8421**	0.80249**	-0.9596**	0.83285**	0.99625**	0.95879**
	10--20	0.09184	0.23739	-0.9019**	0.99964**	0.77707**	0.90779**
	20-30	0.75779**	0.78129**				
Co	0-2	0.83247**	0.88876**	-0.5681	0.78232**	0.41232	0.56441
	2--4	0.82661**	0.89816**	-0.9843**	0.97332**	0.98749**	0.98431**
	4--6	0.74881**	0.77427**	-0.9976**	0.99317**	0.99969**	0.9983**
	6--10	0.69404*	0.76045**	-0.9898**	0.90301**	0.99844**	0.98942**
	10--20	0.40839	0.61387*	-0.843**	0.99554**	0.69514*	0.85033**
	20-30	0.86781**	0.81082**				
Pb	0-2	0.66374*	0.48044	-0.6563*	0.40928	0.78023**	0.65963*
	2--4	0.35831	0.4189	-0.5873	0.63035*	0.5719	0.58745
	4--6	0.64918*	0.5439	-0.9746**	0.96289**	0.98359**	0.97705**
	6--10	0.60035	0.56918	-0.9947**	0.9804**	0.95486**	0.99499**
	10--20	0.29745	0.47905	-0.6605*	0.93021**	0.46826	0.67082*
	20-30	0.70854*	0.67666*				
Cr	0-2	0.76079**	0.77805**	-0.9502**	0.99975**	0.87953**	0.94885**
	2--4	0.58634	0.65121*	-0.9999**	0.99916**	0.99948**	0.99991**
	4--6	0.64271*	0.7515**	-0.998**	0.99986**	0.99412**	0.99717**
	6--10	0.59043	0.63712*	-0.9999**	0.95929**	0.97728**	0.99993**
	10--20	0.60478*	0.71698*	-0.948**	0.98884**	0.84824**	0.95229**
	20-30	0.97842**	0.95218**				

Table C.16b:- Downcore correlation coefficients of various constituents with organic carbon, organic nitrogen and sediment texture

		0-2	2—4	4--6	6--10	10--20	20-30
Na	0-2	1					
	2--4	0.99388**	1				
	4--6	0.94301**	0.96214**	1			
	6--10	0.8123**	0.828**	0.94096**	1		
	10--20	0.90066**	0.91352**	0.94022**	0.90442**	1	
	20-30	0.88499**	0.91311**	0.78869**	0.55191	0.85133**	1
K	0-2	1					
	2--4	0.96788**	1				
	4--6	0.85745**	0.94207**	1			
	6--10	0.642*	0.7742**	0.87306**	1		
	10--20	0.94453**	0.98283**	0.96085**	0.7451**	1	
	20-30	0.60457*	0.60603*	0.2705	0.3273	0.41584	1
Li	0-2	1					
	2--4	0.95963**	1				
	4--6	0.9322**	0.94446**	1			
	6--10	0.94292**	0.96097**	0.99085**	1		
	10--20	0.88654**	0.94719**	0.82957**	0.88035**	1	
	20-30	1	1	1	1	1	1
Ca	0-2	1					
	2--4	0.92666**	1				
	4--6	0.91614**	0.97489**	1			
	6--10	0.94862**	0.84392**	0.731*	1		
	10--20	0.97901**	0.78416**	0.77728**	0.90421**	1	
	20-30	0.99726**	0.95657**	0.97076**	0.98002**	0.98993**	1
Mg	0-2	1					
	2--4	0.98232**	1				
	4--6	0.94836**	0.9412**	1			
	6--10	0.93084**	0.90589**	0.98188**	1		
	10--20	0.93691**	0.9398**	0.9355**	0.95547**	1	
	20-30	0.68527*	0.70542*	0.58229	0.44885	0.39729	1

Table C.17a:- Correlation matrix of major elements between depths

		0-2	2--4	4--6	6--10	10--20	20-30
Fe	0-2	1					
	2--4	0.78216**	1				
	4--6	0.5405	0.79471**	1			
	6--10	0.58876	0.81909**	0.92356**	1		
	10--20	0.36294	0.55849	0.74197**	0.89589**	1	
	20-30	0.47284	0.60167	0.87945**	0.85821**	0.86919**	1
Mn	0-2	1					
	2--4	0.9363**	1				
	4--6	0.88244**	0.97235**	1			
	6--10	0.90968**	0.90614**	0.91021**	1		
	10--20	0.72583*	0.83672**	0.88605**	0.82714**	1	
	20-30	0.63805*	0.7502**	0.75849**	0.62626*	0.91447**	1
Ni	0-2	1					
	2--4	0.88013**	1				
	4--6	0.87899**	0.86386**	1			
	6--10	0.85803**	0.89326**	0.93645**	1		
	10--20	0.79031**	0.82418**	0.92301**	0.97759**	1	
	20-30	0.79588**	0.81476**	0.88359**	0.95021**	0.96684**	1
Cu	0-2	1					
	2--4	0.26533	1				
	4--6	0.76938**	0.17202	1			
	6--10	0.85422**	0.2827	0.90225**	1		
	10--20	0.7859**	0.19722	0.84559**	0.97323**	1	
	20-30	0.73409*	-0.1528	0.66763*	0.8593**	0.91475**	1
Zn	0-2	1					
	2--4	0.00655	1				
	4--6	0.65313*	0.2264	1			
	6--10	0.67334*	0.5436	0.8997**	1		
	10--20	-0.0062	0.50809	0.21572	0.44684	1	
	20-30	0.7988**	-0.0767	0.77144**	0.66543*	0.14771	1
Co	0-2	1					
	2--4	0.86819**	1				
	4--6	0.60367*	0.78426**	1			
	6--10	0.75167**	0.89123**	0.81873**	1		
	10--20	0.32726	0.53244	0.62091*	0.80535**	1	
	20-30	0.57063	0.54603	0.61344*	0.83131**	0.90973**	1
Pb	0-2	1					
	2--4	0.36694	1				
	4--6	0.61569*	0.13309	1			

		0-2	2--4	4--6	6--10	10--20	20-30
	6--10	0.87454**	0.22663	0.5357	1		
	10--20	0.64084*	0.03368	0.30455	0.90751**	1	
	20-30	0.67133*	0.01699	0.40413	0.93594**	0.91845**	1
Cr	0-2	1					
	2--4	0.93948**	1				
	4--6	0.90601**	0.98424**	1			
	6--10	0.91555**	0.95026**	0.94261**	1		
	10--20	0.87637**	0.92005**	0.93877**	0.87923**	1	
	20-30	0.84562**	0.91232**	0.9291**	0.91117**	0.94322**	1

Table C.17b:- Correlation matrix of trace metals between depths

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